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*Organophosphorus*

**Preparation of diphenyl phosphite.**

A. S. Arbuzov and M. G. Imaev (S. M. Kirov Chem. Tech. Inst., Kazan).  
Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 171.

Cf. Noack et al. Ann. 218, 92 (1883); Milebendzki et al., Chem. Polsk.  
15, 66 (1917); Kabachnik et al. Doklady Akad. Nauk SSSR, 115, 512 (1957).

$(\text{PhO})_2\text{P}^+\text{HO}$  may be prepd. by careful hydrolysis of  $(\text{PhO})_3\text{P}$ . Thus, 55 g.

$(\text{PhO})_3\text{P}$  was treated with 3.25 g.  $\text{H}_2\text{O}$  and stirred 15-20 min. during which  
the temp. rose to  $85^\circ$  spontaneously; after 1.5 hrs. on a steam bath the  
resulting 15 g.  $\text{PhOH}$  was removed by vacuum distn. under  $\text{N}_2$ , leaving a  
residue of 100% crude  $(\text{PhO})_2\text{P}^+\text{HO}$ ,  $n_D^{20}$  1.5590. This may be purified by  
distn., although some  $\text{PhOH}$  and red P always forms during a distn.; the  
pure product, 10 g.,  $b_1$   $150-52^\circ$ ,  $n_D^{20}$  1.5595,  $d_{20}$  1.2396. It is very sen-  
sitive to moisture.

esters of  $\beta$ -oxophosphonic acids. 4. Infra-red spectra of the reaction products of  $\alpha$ -halo ketones with triethyl phosphite and diethyl sodium-phosphite.

M. A. Arbutov and M. G. Novsseyan. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 267-71. Cf. this j. 1957, 54, 1959, 41.

The infra-red absorption spectra are shown for the reaction products of appropriate  $\alpha$ -halo ketones with  $(EtO)_3P$  or  $(EtO)_2PONa$ . The presence of the typical carbonyl band (5.84-5.85  $\mu$ ) indicates the normal ketonic structure of  $MeCOCH_2PO(OEt)_2$  prepd. from the reaction with  $(EtO)_3P$ ; the same is true of  $MeCOCH_2PO(OEt)_2$  and  $EtCOCH_2PO(OEt)_2$  prepd. by the similar route. The reaction products of  $AcCH_2Br$  and  $MeCOCH_2Br$  with  $(EtO)_2PONa$ , on the other hand, do not display the carbonyl band and do show the epoxy band at 11.80-11.98  $\mu$ , thus indicating their structures as being those of epoxy phosphonates. The spectra do not provide sufficient basis for estn. of any enolization of the oxophosphonates, since the expected  $POH$  band at 3.7-4  $\mu$  was unobservable. The spectra were detd. with solns. of the esters in  $CCl_4$ , hexane,  $EtOH$  and without solvents.

Organothosphorus

*Organophosphorus*

Diethyl ester of cyclohexanone-2-phosphonic acid.

B. A. Arbuzov, V. S. Vinogradova and N. A. Polezhaeva (State Univ., Kazan).  
Doklady Akad. Nauk S.S.S.R. 128, 81-4(1959).

Reaction of 2-chloro- or -bromocyclohexanone with  $(RO)_3P$  yields the dialkyl cyclohexenyl phosphate. The reaction of bromocyclohexanone with  $(RO)_2P^+ONa$  yields the same product and dialkyl 1,2-epoxycyclohexanephosphonate. However, dropwise addn. of 32 g.  $(EtO)_3P$  to 40 g. 2,6-dibromocyclohexanone, the reaction being completed by 1 hr. at 150-5° and 1 hr. at 185-90°, gave 27.6 g.  $EtBr$  and a range of products,  $b_{2.5}$  48-179°, which on redistn. gave 16.7 g. di-Et 6-diethylphosphono- $\Delta^{1-2}$ -cyclohexenyl phosphate,  $b_{2.5}$  172.5-3°,  $d_4^{20}$  1.1885,  $n_D^{20}$  1.4652. This (12.7 g.) refluxed 2 hrs. with 0.3 g. Na dissolved in 30 ml. abs.  $EtOH$  gave after neutralization with  $AcOH$  some  $(EtO)_3P=O$  and 3.5 g. di-Et 2-cyclohexanonephosphonate,  $b_{3.5}$  119-21°, 1.1258, 1.4654; its MR lies between 57.06 calcd. for the oxo form and 58.1 calcd. for the enol form. It gives a violet color with  $FeCl_3$  and the Meyer bromination-titration indicated some 9% enol in  $EtOH$  and 60% enol in hexane. The Raman spectrum (242(1), 272(1), 337(2), 285(1), 446(1), 479(2), 525(1), 602(3), 658(5), 707(2), 753(2), 792(2), 824(3), 852(5), 900(0), 958(4), 986(0), 1025(3), 1053(0), 1078(1), 1101(3), 1119(2), 1135(2), 1180(4), 1225(1), 1246(1), 1282(2), 1356(2), 1396(1), 1422(6), 1451(7), 1631(7), 1662(0), 1711(3), 2730(2), 2767(0), 2867(5), 2900(3), 2934(6), 2973(4)  $cm^{-1}$ ) indicates the presence of the keto form (1711) and the C=C bond of the enol (1631); the presence of both forms was also shown by the ultraviolet spectrum with maxima at 280 m and 220 m. In basic soln. a max. at 250 m appears due to formation of the enolate ions. I has the Raman spectrum: 645(0), 703(1), 748(2), 805(1), 850(0), 940(0), 1040(0), 1099(3), 1174(0), 1225(1), 1280(1), 1393(0), 1443(3), 1675(3), 2720(1), 2870(3), 2899(2), 2931(5), 2972(5) and 3054(0)  $cm^{-1}$ . Cf. Pudovik et al. Zhur.Obshh.Khim.26,1431(1956); Jacobson et al. JACS 79, 2608(1957).

**Addition of phenylphosphine to unsaturated compounds.**

B. A. Arbuzov, G. M. Vinokurova and I. A. Perfil'eva (Inst. Org. Chem., Acad. Sci., Kazan). Doklady Akad. Nauk S.S.S.R. 127, 1217-20 (1959).  
cf. Mann et al. J.C.S. 1952, 4453, and Doak and Freedman, JACS 74, 3414(1952) and 74, 562(1952).

Heating 13.5 g.  $\text{CH}_2=\text{CHCO}_2\text{Me}$  and 6.1 g.  $\text{PhPH}_2$  6 hrs. at  $120-30^\circ$  gave 55.5%  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2$ ,  $b_1$   $149-50^\circ$ ,  $d_{20}$  1.1388,  $n_D^{20}$  1.5361. Similarly were prepd.: 56.6%  $\text{PhP}(\text{CH}_2\text{CHMeCO}_2\text{Me})_2$ ,  $b_{1.5}$   $139-40^\circ$ , 1.1016, 1.5242; 57.8%  $\text{PhP}(\text{CH}_2\text{CHMeCO}_2\text{Et})_2$ ,  $b_1$   $150-1^\circ$ , 1.0764, 1.5172; 64.6%  $\text{PhP}(\text{CH}_2\text{CHMeCO}_2\text{Pr})_2$ ,  $b_1$   $170-1^\circ$ , 1.0394, 1.5061; 65.7%  $\text{PhP}(\text{CH}_2\text{CHMeCO}_2\text{CHMe}_2)_2$ ,  $b_1$   $152-3^\circ$ , 1.0394, 1.5038; 66.9%  $\text{PhP}(\text{CH}_2\text{CHMeCO}_2\text{Bu})_2$ ,  $b_1$   $185-6^\circ$ , 1.0267, 1.5038; 76.1%  $\text{PhP}(\text{CH}_2\text{CHMeCO}_2\text{CH}_2\text{CHMe}_2)_2$ ,  $b_1$   $178-9^\circ$ , 1.0181, 1.5001; 56.16%  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_2$ ,  $b_1$   $175^\circ$ , 1.1017, 1.5740 (the reaction used allyl alc. and a little  $(\text{Me}_2\text{C}(\text{CN})\text{N})_2$  initiator, 7 hrs. at  $120-30^\circ$ ); reaction of 30.1 g.  $\text{PhPH}_2$  and 49 g.  $\text{CH}_2=\text{CHCN}$  in 3 hrs. at  $90^\circ$  and 6 hrs. at  $120-30^\circ$  gave 48.8%  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CN})_2$ ,  $b_{0.5}$   $176.5-8^\circ$ , 1.1043, 1.5672 (m.  $69-70^\circ$ ) and 7.9%  $\text{PhPHCH}_2\text{CH}_2\text{CN}$ ,  $b_{0.5}$   $104^\circ$ , 1.0710 1.5649, along with 2.04%  $\text{PhP}(\text{O})(\text{CH}_2\text{CH}_2\text{CN})_2$ , m.  $104-5^\circ$ ,  $b_{0.5}$   $235-40^\circ$ . Reduction of 10 g.  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CN})_2$  with 7.2 g.  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$ , the phosphine being held in a Soxhlet thimble above the mixt., gave 48.5%  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$ ,  $b_1$   $144^\circ$ , 1.0292, 1.5728. Addn. of atm. O or heating with S gave the following oxides and sulfides: 73.3%  $\text{PhP}(\text{S})(\text{CH}_2\text{CHMeCO}_2\text{Me})_2$ ,  $b_{0.5}$   $184^\circ$ , 1.1712, 1.5495; 17.1%  $\text{PhP}(\text{O})(\text{CH}_2\text{CHMeCO}_2\text{Et})_2$ ,  $b_1$   $177-8^\circ$ , 1.1128, 1.5123; 18.2%  $\text{PhP}(\text{O})(\text{CH}_2\text{CHMeCO}_2\text{Pr})_2$ ,  $b_{0.5}$   $182-3^\circ$ , 1.0686, 1.5028; 75.3%  $\text{PhP}(\text{S})(\text{CH}_2\text{CHMeCO}_2\text{Bu})_2$ ,  $b_{0.5}$   $205-270^\circ$ (??), 1.0789, 1.5219.

*Organophosphorus*

Esters of phosphoric and thiophosphoric acid containing heterocyclic radicals. 2. Alkylation of some heterocyclic compounds by derivatives of phosphoric and phosphorous acids.

B. A. Arbuzov and V. M. Zoroastrova (State Univ., Kazan). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1037-40 (1959). cf. 1958, 1331, and Zhur. Obshch. Khim. 22, 2041(1952).

Heating 41.5 g. K salt of 4,6,6-trimethyl-6H-1,3-thiazine-2-thiol suspended in  $C_6H_6$  with 33.88 g.  $(EtO)_2POCl$  5 hrs. gave a reddish soln. with a small amt. of KCl; after centrifuging, the soln. was distd. yielding 45.8% ethylation product of 4,6,6-trimethyl-6H-1,3-thiazine-2-thiol,  $C_9H_{15}S_2N$ ,  $b_3$  91-2°,  $d_4^{20}$  1.0497,  $n_D^{20}$  1.5518; the same formed from the above K salt and  $KtI$  in refluxing  $C_6H_6$ . Similar reaction of the K salt with  $(iso-BuO)_2POCl$  gave a low yield of crude 4,6,6-trimethyl-6H-1,3-thiazine-2-thiol  $iso-Bu$  ether,  $b_{3-3.5}$  99-101°,  $n_D^{20}$  1.5370,  $d_4^{20}$  1.0032. Refluxing 9.45 g. K salt of 2-mercaptobenzoxazole with 8.6 g.  $(EtO)_2POCl$  in dry  $Me_2CO$  5 hrs. gave after centrifuging 64.7% 2-ethylmercaptobenzoxazole,  $b_{4.5-5}$  114-15°,  $d_4^{20}$  1.1837,  $n_D^{20}$  1.5940. Oxidation of 2-mercaptobenzoxazole with 5%  $H_2O_2$  in  $AcOH$  at 3-6° gave benzoxazole-2 sulfide, m. 112-3°. This treated with 2 moles  $(EtO)_3P$  in xylene gave an exothermic reaction, completed by 1 hr. on a steam bath, which gave 77.4% I. The above disulfide was treated with  $Cl_2$  in  $MePh$  at -15° and the resulting sulfonyl chloride was treated with  $(EtO)_3P$  at -10°, yielding 36% I. Reaction of K salt of 2-mercaptobenzothiazole with  $(EtO)_2POCl$  in  $MePh$  gave 72% 2-ethylmercaptobenzothiazole, the same being formed in 83.7% yield from benzothiazole-2 disulfide and  $(EtO)_3P$  or  $EtOP(OCH_2)_2$  (41.3% yield).

*Organophosphorus*

**Action of halo-substituted ethers on salts of dialkyl phosphites.**

A.E. Arkharov and V.S. Abramov (Chem. Technol. Inst., Kazan). Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 35-40.

Reaction of  $(EtO)_2PONa$  from 13.5 g. ester and 2.2 g. Na, in  $Et_2O$  with 12.5 g.  $MeOCH_2Br$  rapidly gave 100%  $NaBr$  and 78%  $MeOCH_2P(O)(OEt)_2$ ,  $b_p$  102-105°,  $n_D^{20}$  1.4250,  $d_4^{15}$  1.096. If the  $NaBr$  is not sepd. for distn. of the product, the latter reacts and dissolves it during distn. at about 200° bath temp. in an exothermic reaction which evolved gaseous products; on cooling, the mixture solidified and after pptn. from  $EtOH$  with  $Et_2O$  the product was shown to be  $MeOCH_2P(O)(ONa)OEt$ , m. 176-77°. Reaction of  $(EtO)_2PONa$  from 19 g. ester and 2.2 g. Na in  $Et_2O$ , with 9.5 g.  $MeOCH_2Cl$  was quite slow and gave ~~mainly~~  $MeOCH_2P(O)(OEt)_2$  along with some  $(EtO)_2P$ . To a soln. of  $(EtO)_2PONa$  in  $Et_2O$ , contg. 0.15 g. Na, was added 2.5 g.  $(PhO)_2P-GuBr$  adduct after which 0.5 g.  $MeOCH_2Cl$  was added and the whole heated briefly; the pptd.  $NaCl$  was sepd. and the filtrate on evapn. gave only  $(PhO)_2P-GuBr$  adduct.  $(MeO)_2PONa$  and  $MeOCH_2Br$  in  $Et_2O$  gave 40%  $MeOCH_2P(O)(OMe)_2$ ,  $b_p$  91-2°,  $n_D^{20}$  1.4250. Use of  $MeOCH_2Cl$  gave unstated yield of the same product,  $b_p$  91-1.5°,  $n_D^{20}$  1.4238,  $d_4^{15}$  1.1898. Heating 11 g.  $(MeO)_2POAg$  and 6.3 g.  $MeOCH_2Br$  in  $C_6H_6$  resulted in soln. of the Ag salt, followed by pptn. of 8 g.  $AgBr$ ; distn. gave unstated yield of  $MeOCH_2P(O)(OMe)_2$ ,  $b_p$  91-2°, 1.4200, 1.1899 and a little  $AgBr$  residue. If the solvent is carefully distd. from the reaction mixture, the viscous residue is an adduct which yields  $AgBr$  at 110-15°. Reaction of 20 g.  $(EtO)_2POAg$  and 6.6 g.  $MeOCH_2Cl$  in  $C_6H_6$  gave some free Ag and a ppt.; the yellow soln. was decanted and distd. yielding a residue of 12 g.  $AgCl$ , 2.7 g.  $(EtO)_2P$ , and 4 g. product,  $b_p$  46-48°, which gave an exothermic reaction with  $CuX$  but failed to give a solid adduct. Reaction of  $(BuO)_2POAg$  with  $MeOCH_2Cl$  gave crude mixed esters of  $H_2PO_3$  (test with  $CuI$ ):  $b_{10}$  80-115°, a product,  $b_{10}$  115-30°, and  $AgCl$ . To 2.4 g.  $(EtO)_2POAg$  in  $C_6H_6$  was added 1.3 g.  $MeOCH_2Br$ , the mixture was heated until the ppt. had dissolved, and the soln. decanted from the ppt. was treated with 2 g.  $Ph_3GBr$  yielding 1.5 g.  $AgBr$  and an oil, which heated with  $HCl$ .

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in a sealed tube gave  $\text{Ph}_3\text{COH}$ . Similarly, the use of  $\text{MeOCH}_2\text{Cl}$  gave  $\text{AgCl}$  and an unrefractable mass which with  $\text{HCl}$  gave  $\text{Ph}_3\text{CP}(\text{O})(\text{OH})_2$ , m.  $270-72^\circ$ . Addn. of 1 g.  $\text{Ph}_3\text{CBr}$  in  $\text{C}_6\text{H}_6$  to 1 g. of adduct of  $\text{AgBr}$  and  $(\text{EtO})_3\text{P}$  gave after heating, some  $\text{AgBr}$  and a liquid which on concn. gave  $\text{Ph}_3\text{CP}(\text{O})(\text{OEt})_2$ , m.  $120-21^\circ$ .  $\text{Ph}_3\text{CBr}$  reacts with  $(\text{EtO})_3\text{P}$  in hot  $\text{C}_6\text{H}_6$  and gives the same ester. Evidently,  $\text{MeOCH}_2\text{Cl}$  tends to yield mixed esters of  $\text{H}_3\text{PO}_3$ .

27.3  
29.1



g *Organic*

Esters of  $\beta$ -keto phosphonic acids. 3. Structure of reaction products of some halogenated ketones with triethyl phosphite and sodium diethyl phosphite.

B.A. Arbuzov, V.S. Vinogradova and N.A. Poleshaeva (State Univ., Kazan).

Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 41-49. Cf. Doklady Akad. Nauk SSSR, 99, 85 (1954), 106, 283 (1955), 106, 465 (1956), 111, 107 (1956), and this j. 1957, 54 and 284.

Reaction of 46.8 g.  $(EtO)_2PHO$  with 7.4 g. Na in  $Et_2O$  gave the Na salt which was slowly treated with 30 g.  $MeCOCH_2Cl$  at b.pt. of the solvent; after heating on a steam bath, the NaCl was sepd. by centrifuging, and the product was distd. yielding 18 g.  $(EtO)_2P(O)CH_2CO_2Me$  (I),  $b_p$  91°,  $n_D^{20}$  1.4517,  $d_4^{20}$  1.1154, and 9 g.  $(EtO)_2P(O)CH_2CO_2Ac$  (II),  $b_{1.5}$  101-103°, 1.4548, 1.1115, which gave a 2,4-dinitrophenylhydrazone, m. 104-105° (cf. Kreutshamp and Kayser, Ber., 89, 1614 (1956); present authors could not duplicate the isolation of the isopropenyl ester described by these authors). Similar reaction of  $(EtO)_2PONa$  from 36 g.  $(EtO)_2PHO$  in  $Et_2O$  with 34.2 g.  $BrCH_2COMe$  gave unstated yield of I,  $b_{p,5}$  111°, 1.4513, 1.1141, and II,  $b_{p,5}$  107-112°, 1.4547, 1.1119 which gave the dinitrophenylhydrazone, m. 104-105°. Carefully fractionated  $AcCH_2P(O)(OEt)_2$ , prepd. ~~likewise~~ by the Arbuzov method ~~was shown to be an individual substance with~~  $b_p$  109°,  $d_4^{20}$  1.1153,  $n_D^{20}$  1.4546. The similar product prepd. with  $(EtO)_2PONa$  had  $b_{p,5}$  86°, 1.1152, 1.4517, which was actually I rather than II. Its formation may be explained by reaction of the Na salt at the carbonyl group rather than at the Br atom. The Raman spectrum of I is (in  $cm^{-1}$ ): 285(5), 326(3), 483(3), 527(1), 627(2), 638(4), 749(4), 796(4), 810(2), 851(4), 923(3), 993(2), 1027(1), 1069(1), 1100(4), 1160(2), 1217(3), 1266(3), 1290(2), 1350(3), 1381(2), 1397(2), 1452(7), 1478(2), 2725(1), 2870(2), 2904(3), 2932(5), 2983(4), 3061(1). The C=O and C=C lines are absent and the 1266 line of epoxy ring is present. This spectrum was the same as that produced by the I prepd. by dehydrochlorination of  $ClCH_2COMe(OH)P(O)(OEt)_2$ . Reaction of  $AcCH_2Br$

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with  $(\text{EtO})_3\text{P}$  gave I and  $(\text{EtO})_2\text{P}(0)\text{OCMe:CH}_2$ , whose Raman spectrum was: 299(1), 470(1), 521(0), 707(5), 751(2), 814(1), 860(1), 911(1), 1034(3), 1070(1), 1100(3), 1162(1), 1289(4), 1371(3), 1397(4), 1447(3), 1457(3), 1478(1), 1662(6), 2729(2), 2870(3), 2901(2), 2931(6), 2974(5), 3003(4), which is rather similar to that of  $\text{Et}_3\text{PO}_4$  but ~~has~~ has the C:O line at 1662. Raman spectrum of II is: 237(3), 268(3), 323(2), 455(3), 532(2), 593(3), 667(0), 718(6), 768(1), 791(1), 819(3), 851(2), 961(1), 1028(2), 1101(5), 1128(1), 1165(1), 1200(1), 1257(3), 1293(3), 1368(1), 1398(3), 1425(1), 1451(5), 1480(2), 1638(1), 1715(4), 2725(2), 2775(2), 2872(4), 2900(5), 2926(3), 2973(6), 3000(2). Reaction of  $(\text{iso-PrO})_2\text{POMe}$  and  $\text{ClCH}_2\text{Ac}$  gave  $(\text{iso-PrO})_2\text{P}(0)\text{CH}_2\text{Ac}$ ,  $b_{2.5}$   $94^\circ$ ,  $d_{20}^{20}$  1.1154,  $n_D^{20}$  1.4517; use of  $\text{BrCH}_2\text{Ac}$  gave the same epoxy deriv.  $b_{9.5}$   $111^\circ$ , 1.1141, 1.4513. In both cases some  $(\text{iso-PrO})_2\text{P}(0)\text{CH}_2\text{Ac}$  was formed,  $b_{1.5}$   $101-103^\circ$ , 1.1115, 1.4548. Reaction product of  $(\text{EtO})_3\text{P}$  with  $\text{EtCOCH}_2\text{Br}$  is evidently an ester of  $\alpha$ -keto-butylphosphonic acid with Raman spectrum: 268(2), 324(2), 403(1), 455(2), 553(1), 614(1), 668(1), 711(7), 793(4), 820(3), 867(2), 949(2), 1028(3), 1054(2), 1101(6), 1164(1), 1200(1), 1256(3), 1290(4), 1363(2), 1405(5), 1453(6), 1477(4), 1634(1), 1715(6), 2725(2), 2768(1), 2875(3), 2903(5), 2936(8), 2978(6). Methylation of K deriv. of II or its Me deriv. yields products which have the structure of II: mono-Me deriv. has the Raman spectrum 297(3), 412(2), 504(1), 614(3), 652(2), 694(4), 709(2), 751(2), 794(2), 813(3), 941(0), 969(0), 1024(0), 1059(1), 1098(4), 1164(1), 1203(1), 1249(1), 1289(2), 1395(1), 1451(1), 1712(5), 2901(2), 2932(5), 2978(3), and the di-Me deriv.: 295(2), 357(2), 438(1), 570(1), 598(1), 654(5), 695(2), 744(2), 791(3), 808(2), 899(3), 960(3), 1025(2), 1099(4), 1124(1), 1163(2), 1247(3), 1291(2), 1366(2), 1390(2), 1453(5), 1473(2), 1707(5), 2876(2), 2903(1), 2930(3), 2930(4). The reaction product of  $(\text{EtO})_2\text{POMe}$  with  $\text{MeCOCHMeMe}$  lacks the C:O line in the spectrum and that of C:C, which indicates that the substance is an epoxy deriv., ester of epoxyisobutylphosphonic acid. Its Raman spectrum is: 284(3), 332(3), 478(3), 503(1),

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541(2), 633(2), 647(5), 741(7), 770(1), 796(1), 812(1), 838(5), 909(4), 948(1), 989(2), 1028(3), 1069(0), 1100(7), 1115(2), 1146(1), 1163(1), 1203(2), 1261(3), 1289(2), 1301(5), 1370(1), 1395(1), 1413(3), 1452(6), 1479(2), 2720(1), 2769(1), 2871(4), 2903(3), 2934(6), 2980(5), 3005(3), 3061(1). This does not form a dinitrophenylhydrazones. The deriv. of authentic II gives (III) 2,4-dinitrophenylhydrazones, m. 110-15°. Reaction product of  $\text{NaCOOCH}_2\text{Me}_2$  and  $(\text{EtO})_2\text{PNa}$  or  $(\text{EtO})_2\text{P}$  is not too well characterized by Raman spectra as both products gave C=O bands that were displaced from normal (1699 and 1700 instead of 1707  $\text{cm}^{-1}$ ). The di-Me deriv. of II prepared by Arbuzov reaction had the Raman spectrum: 332(1), 511(1), 548(2), 579(4), 639(6), 749(5), 812(2), 837(1), 965(2), 1011(3), 1035(2), 1066(1), 1100(5), 1163(1), 1286(4), 1376(2), 1394(4), 1450(6), 1475(1), 1699(5), 2452(0), 2726(2), 2777(2), 2865(4), 2905(2), 2932(5), 2981(5), 3004(2). The di-Me deriv. of I prep'd. via the Na salt of the ester had Raman spectrum: 236(3), 334(2), 397(1), 479(2), 521(3), 548(1), 577(3), 631(5), 653(1), 686(6), 751(5), 798(2), 813(4), 868(5), 946(2), 975(3), 1024(3), 1058(0), 1099(6), 1164(1), 1230(3), 1261(1), 1283(4), 1356(4), 1378(1), 1391(5), 1451(7), 1480(4), 1700(6), 2453(1), 2739(2), 2773(1), 2868(4), 2903(4), 2929(6), 2976(4), 3006(2), 3035(2). The absorption spectrum of III is different from that of di-Me deriv. of II prep'd. by methylation of II; III lacks the carbonyl group band. The true structure of III remains unclear. Reaction of  $(\text{EtO})_2\text{PNa}$  with  $\text{NaCOOCH}_2\text{CH}_2\text{OH}$  failed to yield the expected product since undistillable products formed either through polymerization of the possible vinyl ketone or for other reasons. The reaction with  $\text{NaCO}(\text{CH}_2)_5\text{OH}$  gave a good yield of a product with  $b_{3.5}$  108-10°,  $d_4^{20}$  1.0898,  $n_D^{20}$  1.4432; its Raman spectrum/as: 276(2), 304(2), 586(2), 614(4), 700(2), 723(6), 757(1), 792(3), 809(2), 836(4), 861(4), 911(2), 927(6), 1003(4), 1034(4), 1099(6), 1159(4), 1204(4), 1244(5), 1253(2), 1293(3), 1353(2), 1366(3), 1451(6), 1480(3), 2725(1), 2773(0), 2869(3), 2906(5), 2933(6), 2978(4), 3006(2), which agrees with formulation of di-Et 2-methyl-2-tetrahydrofuranphosphonate (cf. Arbuzov et al. Zhur.Obshh.Khim.29, 1463(1930) where the product was described as oxopentylphosphonate).

**Action of triarylmethyl halides on silver salts of dialkyl phosphites.**

A.E.Arbuzov and E.A.Krasil'nikova (Chem. Technol. Inst., Kazan). Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 30-34.

Reaction of  $(RO)_2POAg$  with  $Ar_3CX$  was examined.  $(MeEtCHO)_2PHO$ , prep'd. for the first time, had  $b_{14}$  103-104°,  $n_D^{20}$  1.4190,  $d_4^{20}$  0.9754. The Ag salts were prep'd. by previously described technique (Arbuzov, Selected Works, Moscow, 1952). Heating 4.89 g.  $(iso-PrO)_2POAg$  with 6.84 g.  $o-ClC_6H_4COI$  ( $C_6H_4Cl-p$ )<sub>2</sub> (I) in  $C_6H_6$  0.5 hr. on a steam bath gave after filtration of AgCl, reheating to boiling, filtration of addnl. AgCl, and evapn. 21.29%  $(iso-PrO)_2POC(C_6H_4Cl-o)(C_6H_4Cl-p)_2$ , m. 128-29° (from petr. ether), which with dil. HCl at 150° in 3 hrs. gave  $Ar_3COH$ . Ag salts of Et, iso-Bu, iso-Pr and sec-butyl phosphites react similarly with  $Ar_3COI$  and yield the mixed esters of  $H_3PO_3$ , i.e.  $(RO)_2POAr$  Ag salts of phosphites with primary radicals (except the Et noted above) react with  $Ar_3COH$  and yield esters of phosphonic acids. These were also prep'd. for comparison from  $(RO)_3P$  and the desired halide. The following are reported:  $(EtO)_2P(O)C(C_6H_4Cl-o)(C_6H_4Cl-p)_2$ , m. 116-17°;  $(EtO)_2P(O)C(C_6H_4Me-p)_3$ , m. 127-29°;  $(iso-PrO)_2P(O)C(C_6H_4Cl-o)(C_6H_4Cl-p)_2$ , m. 190-91°;  $(iso-PrO)_2P(O)C(C_6H_4Me-p)_3$ , m. 108-10°;  $(MeEtCHO)_2P(O)C(C_6H_4Cl-o)(C_6H_4Cl-p)_2$ , m. 110-11°;  $(iso-BuO)_2P(O)C(C_6H_4Cl-o)(C_6H_4Cl-p)_2$ , m. 107-108°;  $(iso-BuO)_2P(O)C(C_6H_4Me-p)_3$ , m. 94-95°. If the Ag salt of the phosphite contains secondary alkyl groups, the reaction with  $Ar_3COH$  yields  $(RO)_2POAr$ , i.e. an ester of  $H_3PO_3$ . Reaction without heating gives the same results as one with heating; keeping a sealed tube with  $(EtO)_2POAg$  and I 15 days in  $Et_2O$  gave the oily phosphite ester which with HCl readily gave  $H_3PO_3$  and the arylcarbinol. Cl in the aryl group of triarylmethyl halide tends to yield the mixed phosphite esters, while Me substituent tends to produce phosphonate esters; in this case either triarylmethyl chloride or bromide gave the same results in boiling  $C_6H_6$ . The mixed phosphites were thick undistillable oils and their formation was established only indirectly. The phosphonates, on the other hand, were readily crystallizable solids.

*a* Organophosphorus

**Reaction of phosgene and oxalyl chloride with esters of phosphorous acid.**

**A. N. Pudovik and R. N. Platonova (State Univ., Kazan). Zhur. Obshchei Khim. 29, 507-10 (1959). Cf. Kabachnik et al., Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1945, 364, 597; 1947, 163; and especially 1957, 48 and 1958, 1938.**

**Passage of dry  $\text{COCl}_2$  through  $(\text{RO})_3\text{P}$ , with or without water-cooling, or addn. of  $(\text{RO})_3\text{P}$  to liq.  $\text{COCl}_2$  cooled with a freezing mixt., followed by stirring 0.5 hr. and a vacuum distn. resulted in 60-70%  $(\text{RO})_2\text{POCl}$ . The reaction was run with specimens of  $(\text{RO})_3\text{P}$  in which  $\text{R}=\text{Me}$ ,  $\text{Et}$ ,  $\text{Bu}$ , or  $\text{iso-Bu}$ . Thus were prepd.  $(\text{RO})_2\text{POCl}$ : (R shown)  $\text{Me}$   $b_p$  64.5-5°,  $n_D^{20}$  1.4119,  $d_{20}$  1.3396;  $\text{Et}$ ,  $b_p$  78.5°, 1.4180, 1.1999;  $\text{Bu}$ ,  $b_{11}^{120^\circ}$  1.4312, 1.0760;  $\text{iso-Bu}$ ,  $b_p$  110-10.5°, 1.4268, 1.0699. The products were identical with those formed by chlorination of  $(\text{RO})_2\text{PHO}$ . Evidently the reaction with  $\text{COCl}_2$  yields the above chlorides along with  $\text{CO}$  and  $\text{RCl}$ . To 30 g.  $(\text{COCl})_2$  in 100 ml.  $\text{Et}_2\text{O}$  there was added with cooling 40 g.  $(\text{EtO})_3\text{P}$  and after 1 hr. on a steam bath, the mixt. yielded 12.7 g.  $(\text{EtO})_2\text{POCl}$ . The reaction with  $(\text{MeO})_3\text{P}$  gave a similar result; this reaction yields  $\text{RCl}$  and 2 moles of  $\text{CO}$ . Reaction of  $(\text{EtO})_3\text{P}$  with maleic chloride occurs very violently and yields only tars even in solvents. Also cf. Bandler and Grieco, Z. allgem. anorg. Chem. 290, 258 (1957).**

*Organophosphorus*

addition of partial esters of phosphorus acids to nitroisobutylene and ethyl vinyl sulfone.

A. A. Rudovik and F. N. Sitdikova (State Univ., Kazan). Doklady Akad. Nauk SSSR. 125, 826-8 (1959).

$(\text{RO})_2\text{P}(\text{O})\text{H}$  add readily to  $\text{Me}_2\text{CHCH}:\text{CHNO}_2$  in the presence of  $\text{KOH}$  catalyst and caused considerable heat evolution. Thus were prepd. 56%  $\text{Me}_2\text{CHCH}(\text{CH}_2\text{CO}_2\text{Et})\text{P}(\text{O})(\text{OEt})_2$ ,  $b_p$   $130^\circ$ ,  $n_D^{20}$  1.4503,  $d_{20}$  1.1740, and 37%  $\text{Me}_2\text{CHCH}(\text{CH}_2\text{NO}_2)\text{P}(\text{O})(\text{OEt})_2$ ,  $b_p$   $144^\circ$ , 1.4480, 1.1218.  $(\text{RO})_2\text{P}(\text{O})\text{H}$  was warmed with  $\text{Et}_3\text{N}$  and distd. directly before the reaction which yielded 27%  $\text{Me}_2\text{CHCH}(\text{CH}_2\text{NO}_2)\text{P}(\text{O})(\text{OMe})_2$ ,  $b_p$   $131.5^\circ$ , 1.4087, 1.1901. The reaction with  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$  required much  $\text{KOH}$  and lasting several hours at  $100-10^\circ$  in forming 40%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CH}(\text{CH}_2\text{NO}_2)\text{CHMe}_2$ ,  $b_p$   $170^\circ$ , 1.4872, -. Attempts to add  $(\text{RO})_2\text{P}(\text{O})\text{H}$  and  $(\text{RO})_2\text{P}(\text{O})\text{H}$  to nitrostyrene and furylnitroethylene, even in the presence of mild bases such as piperidine or  $\text{Et}_3\text{N}$ , resulted in polymerization of the olefins and no adducts could be isolated. Reaction of  $\text{CH}_2:\text{CHNO}_2$  with the above substances in the presence of  $\text{KOH}$  gave: 70%  $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_p$   $130^\circ$ ; 51%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{1.5}$   $134^\circ$ , 1.4632, 1.2209; 54%  $(\text{PrO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_p$   $190^\circ$ , 1.4626, 1.1523; 32%  $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_p$   $208^\circ$ , 1.4596, 1.1091; 46%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_p$   $133^\circ$ . Also produced by similar addn. was 40%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{2.5}$   $204^\circ$ . The substances above for which only the b.p. is listed, crystallized or solidified on standing (no m.p. cited). Reaction of the sulfones with  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$  proceeded so energetically that only tar was formed.



C Organophosphorus

Reactions of aldehydes and ketones with oxides of phosphorous acid esters.

V. S. Abramov and M. A. Ilyin (S.M. Kirov Chem. Technol. Inst., Kazan).

Doklady Akad. Nauk S.S.S.R. 125, 1027-9 (1959).

Reaction of aldehydes and ketones with  $\text{e-C}_6\text{H}_5\text{O-PHPh}$  proceeds probably through an adduct of anion type,  $\text{e-C}_6\text{H}_5\text{O-P}^-(\text{NHPh})\text{CHHO}^-$ , which rearranges to the final product  $\text{e-C}_6\text{H}_5\text{O-P(=O)(NHPh)CHHO}$ . The reaction starts with mixing of the reactants and is exothermic. If no attempt to control the temp is made, the products are yellow; with gradual mixing, the products remain colorless. Compounds were prepd.  $\text{e-C}_6\text{H}_5\text{O-P(=O)(NHPh)CHHO}$  (R shown): Me, m. 145-5° (from dioxane); Et, m. 149.5-50.5° (from EtOH); Ph, m. 182-3° (from EtOH);  $\text{Me}_2$ , m. 173-4° (washed with starting material,  $\text{Me}_2\text{CO}$ );  $(\text{CH}_2)_5$ , m. 156-7° (from EtOH). Reaction with  $\text{PhNH-P(=O)(OPh)}_2$  (cf. Kabachnik et al, this j. 96, 991(1954)) with BzH gave  $(\text{PhO})(\text{PhNH})\text{P(=O)CH(OPh)Ph}$ , m. 149-50° (from EtOH); similarly cyclohexanone gave  $(\text{PhO})(\text{PhNH})\text{P(=O)C(OPh)(CH}_2)_5$ , m. 157-8° (from EtOH). The structural formulas of the products are given provisional, on the assumption that a form of Arbusov rearrangement is involved in the reaction. Hydrolysis of the products with dil. HCl yielded only catechol or PhOH and  $\text{PhNH}_2$ ; no hydroxyphosphonic acids were isolated.

d Oxyphosphorus

Reaction of glycerol  $\alpha, \gamma$ -dichlorohydrin with  $\text{PCl}_3$ ,  $\text{POCl}_3$ , and  $\text{PbCl}_2$ .

B. V. Kusnetsov and R. E. Valetdinov (S. M. Kirev Chem. Tech. Inst., Kazan). Zhur. Obshchei Khim. 29, 235-8 (1959). cf. Cook et al. J. Chem. Soc. 1945, 873, and Jones et al. J. Chem. Soc. 1946, 824.

Addn. of 154.8 g.  $\text{HOCH}(\text{CH}_2\text{Cl})_2$  at  $30^\circ$  to 164.4 g.  $\text{PCl}_3$ , followed by stirring 1 hr. and a distn. gave a range of fractions which yielded: 44.9%  $(\text{ClCH}_2)_3\text{P}(\text{X})\text{O}$ ,  $\text{b}_{11}$  95-6°,  $d_{20}$  1.5118,  $n_D^{20}$  1.5310, 40.1%  $[(\text{ClCH}_2)_3\text{CHO}]_2\text{P}(\text{X})\text{O}$ ,  $\text{b}_{0.1}$  126-7°, 1.4891, 1.5193, and 14.4%  $[(\text{ClCH}_2)_3\text{CHO}]_2\text{P}(\text{O})\text{CH}_2\text{CHClCH}_2\text{Cl}$ ,  $\text{b}_{0.07}$  175-8°, 1.5010, 1.5135. The latter heated with concd.  $\text{HCl}$  10 hrs. at  $150^\circ$  and evapd. gave a crystalline Ba salt of the free acid  $\text{C}_7\text{H}_9\text{O}_3\text{PbCl}_2$ . The phosphonate evidently formed through internal isomerization of the expected trialkyl phosphite. Treatment of 13.1 g. I in  $\text{Ba}_3\text{O}$  with 0.73 g.  $\text{H}_2\text{O}$  and 3.2 g. pyridine at  $-5^\circ$  gave after filtration and distn. 61.5%  $[(\text{ClCH}_2)_3\text{CHO}]_2\text{P}(\text{X})\text{O}$ ,  $\text{b}_{0.4}$  145-7°, 1.4805, 1.5010. Addn. of 25.8 g.  $\text{HOCH}(\text{CH}_2\text{Cl})_2$  at  $100^\circ$  to 20.6 g.  $\text{POCl}_3$  and stirring 2.5 hrs. at  $130^\circ$  gave some 18 g.  $(\text{ClCH}_2)_3\text{CHO}-\text{POCl}_2$ ,  $\text{b}_{11}$  122-4°, 1.5300, 1.4885, and some 10 g.  $[(\text{ClCH}_2)_3\text{CHO}]_2\text{P}(\text{X})\text{O}$ ,  $\text{b}_2$  180-2° with decompn. (treated with  $\text{PhNH}_2$  it gave the corresponding anilide, m. 80-1°); the residual  $\text{H}_3\text{PO}_4$  could not be distd. owing to decompn. Addn. of 32.2 g.  $(\text{ClCH}_2)_3\text{CHO}$  to 42.5 g. boiling  $\text{POCl}_3$  and heating 1 hr. at  $150^\circ$  gave a mixt. which failed to yield any definite products on distn.; only some ill-smelling decompn. products were secured.



**Addition of neutral esters of phosphorous and phosphinic acids to conjugated systems. VII. Telomerization of methacrylic acid with trialkyl phosphites.**

**V. A. Kukhtin, G. Kamai, L. A. Sinchenko and K. M. Grekheva (Chem. Technol. Inst., Kazan). Zhur. Obshchei Khim. 29, 510-15 (1959). Cf. 28,1196(1958) and 28, 2790(1958). Also Connell and Coover, JACS 78, 4453 (1956).**

**Keeping 8.3 g.  $(EtO)_3P$ , 21.5 g.  $CH_2:CHCO_2H$  and 0.03 g.  $Ba_2O_2$  3 hrs. at room temp. gave 3.1 g. pptd. telomer, augmented by 0.7 g. more formed overnight.**

**The product, a colorless solid was sol. only in warm  $EtOH$  or  $MeOH$  and  $AcOH$ . Similarly were prepd. telomers of these monomers in various proportions with  $Ba_2O_2$ ,  $NaOH$ ,  $iso-AmI$  or  $Et_3N$  catalysts, as well as telomers employing  $(PrO)_3P$ ,  $(BuO)_3P$  and the initial adduct of  $CH_2:CHCO_2H$  and  $(EtO)_3P$ . These**

telomers contained free  $\text{CN}_2\text{H}$  groups and could be titrated with base in the presence of phenolphthalein ( this and the results of P analysis were used to est. the mol. wts. which ranged from a few hundred to approximately 200. The telomers did not have definite m. pts. but charred on being heated. In general the mol. wt of the telomers rose with increased proportion of the  $\text{CN}_2:\text{CNMeCO}_2\text{H}$  monomer and with increased concn. of the initiating catalysts. The tendency to enter the reaction among the phosphites declines with increasing mol. wt. of radical R. The reaction of  $(\text{EtO})_3\text{P}$  with  $\text{CN}_2:\text{CNMeCO}_2\text{H}$  failed to yield any polymer and gave only the products of the Arbuzov reaction. The results suggest that the original adduct (1:1) of the monomers which is evidently  $(\text{RO})_3\text{P}^+\text{CN}_2\text{CNMeCO}_2\text{H}^-$ , probably is the chain-initiating link in the telomerization. The mechanism of the reaction is discussed.

b

Organophosphorus

Addition of neutral esters of phosphoric acid to p-benzoquinone.

V. A. Kukhtin and K. M. Orskova (All Union Cinc-Photo Res. Inst., Kazan Section ). Doklady Akad. Nauk SSSR, 124, 819-21 (1959).

Of. this j. 109, 91(1956); Zhur. Obshch. Khim. 27, 2372 (1957) and 28, 1196 (1958). Also, Ramirez et al. JACS 78, 5614(1956), J. Org. Chem. 22, 857(1957), 23, 778 (1958); Horner et al. Ber. 91, 58 (1958).

Gradual addn. of  $(RO)_3P$  to a  $C_6H_6$  soln. of p-benzoquinone with cooling to 60-70° resulted in the products listed below. Acid hydrolysis of these gave mainly hydroquinone; hydrolysis with aq. alc. base also resulted in the loss of the P residue. These facts and the detection of a free phenolic group in the products indicated that these are 2,5-(RO)(HO) $C_6H_4P(O)(OR)_2$ ; the following are described (R shown): R= Me,  $b_p$  162-65°,  $n_D^{20}$  1.4850,  $d_4^{20}$  1.2423; Et,  $b_p$  162-65°, 1.4670, 1.1531; Pr,  $b_p$  175-76°, 1.4820, 1.1416. The yields were 51-65%. These are not esters of phosphoric acid since the reaction of  $(EtO)_3POCl$  with p-HOC $_6H_4$ ONt gave  $(EtO)_2P(O)OC_6H_4ONt-p$ , 72%,  $b_p$  150-51°, 1.4805, 1.1351, which differed from the material obtained by the addn. of  $(EtO)_3P$  to the quinone. It is possible however that the phosphorus group may be located o- to the OH group rather than to OR group, in the 3 products described above. It is suggested that the reaction goes through an Arbuzov-type intermediate adduct with a possibly polar link between P and the O-atom of the quinone, which then rearranges to the phosphonate.  $(PhO)_3P$  failed to react at room temp.; on heating in  $C_6H_6$  a red color developed and a ppt. formed; this was a colorless solid which turned to red tar in air and had a phenolic odor; it decomposed at 70-75° yielding a red tar; abs. EtOH gave a red tar and a phenol. The liquid portion of the mixture gave only some PhOH on distn. Analysis of the above solid indicated that it is an Arbuzov-type adduct of  $P(OPh)_3$  and p-benzoquinone; the 2nd phase of the Arbuzov reaction of this substance gave only a tar. Paramagnetic resonance measurements during these reactions failed to show the presence of radicals; diphenylpicrylhydrazyl also showed the absence of radicals. Reaction of chloranil and  $(EtO)_3P$  however displays evidence of radicals.

*Organophosphorus*

Derivatives of  $\gamma$ ,  $\delta$ -dichlorovinyl ester of ethylphosphonic acid.

B. I. Rizpolozhenskii and H. A. Zvereva (A. E. Arbuzov Chem. Inst., Acad. Sci., Kazan). Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 358-60.

Cf. A. E. Arbuzov et al. this J. 1951, 531; 1952, 864; 1953, 1021.

Under  $\text{CO}_2$  atm. 13.9 g.  $\text{CCl}_3\text{CHO}$  in 25 ml.  $\text{C}_6\text{H}_6$  was treated dropwise with 11.5 g.  $\text{EtP}(\text{OMe})_2$  in 15 ml.  $\text{C}_6\text{H}_6$  at  $-10^\circ$ ; after 1 hr. at room temp., the mixture was refluxed 30-40 min. and distd. yielding 16 g.  $\text{EtP}(\text{O})(\text{OMe})\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  63-66°,  $d_{20}$  1.3333,  $n_D^{20}$  1.4680. Similarly were prepd.: 67.5%  $\text{EtP}(\text{O})(\text{OEt})\text{OCH}:\text{CCl}_2$ ,  $b_1$  71-72°, 1.2734, 1.4637; 68%  $\text{EtP}(\text{O})(\text{OPr})\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  83-86°, 1.2214, 1.4620; 75%  $\text{EtP}(\text{O})(\text{OCHMe}_2)\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  73-74°, 1.2260, 1.4575; 68.5%  $\text{EtP}(\text{O})(\text{OBu})\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  92-95°, 1.2002, 1.4624; 73%  $\text{EtP}(\text{O})(\text{OCH}_2\text{CHMe}_2)\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  89-90°, 1.1899, 1.4570; 70.5%  $\text{EtP}(\text{O})(\text{OAm})\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  100-101°, 1.1672, 1.4391; 82.5%  $\text{EtP}(\text{O})(\text{OCH}_2\text{Ph})\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  132-33°, 1.2805, 1.5220; 82.8%  $\text{EtP}(\text{O})(\text{OCH}_2\text{CH}:\text{CH}_2)\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  76-78°, 1.2623, 1.4740. Similar use of appropriate  $\text{EtP}(\text{OR})\text{NR}'_2$  similarly gave: 52%  $\text{EtP}(\text{O})(\text{OCH}:\text{CCl}_2)\text{NMe}_2$ ,  $b_2$  80-82°, 1.2482, 1.4714; 50%  $\text{EtP}(\text{O})(\text{OCH}:\text{CCl}_2)\text{-NMe}_2$ ,  $b_1$  92-93°, 1.1974, 1.4738.  $\text{Et}_2\text{POMe}$  gave 70%  $\text{Et}_2\text{P}(\text{O})\text{OCH}:\text{CCl}_2$ ,  $b_{0.5}$  81-83°, 1.2465, 1.4610. Preliminary tests showed that these products have a high order of biological activity and are being tested further. The intermediates used, prepd. by known methods, included new esters:  $\text{EtP}(\text{OCH}_2\text{Ph})_2$ ,  $b_{1.5}$  140-41°, 1.0761, 1.5499;  $\text{EtP}(\text{OCH}_2\text{CH}:\text{CH}_2)_2$ ,  $b_{11}$  65-67°, 0.9596, 1.4553;  $\text{EtP}(\text{OAm})_2$ ,  $b_2$  81-82°, 0.8834, 1.4390; also listed are:  $\text{EtPNMe}_2\text{Cl}$ ,  $b_{16}$  51-52°, 1.0271, 1.4855 and  $\text{EtPNMe}_2(\text{OCHMe}_2)$ ,  $b_{27}$  71-73°, 0.8932, 1.4377.

*Organosilicon*

Synthesis of hetero-organic compounds of general formula  $M_n(OSiR_3)_n$ .

B. I. Yakovlev and N. V. Vinogradova. Zhur. Obshchei Khim. 29, 695-6 (1952).

Reaction of 6.5 g.  $Ti(OEt)_4$  and 19.6 g.  $Et_3SiOH$  gave 8.3 g.  $(Et_3SiO)_4Ti$ ,  $b_{3.5}$  199-202°,  $d_4^{20.5}$  0.917, dielectric constant 2.18 at 20° at 1000 cps.

Reaction of 2 g.  $B_2O_3$  and 25 g.  $Et_3SiOH$  gave 9.2 g.  $B(OSiEt_3)_3$ ,  $b_3$  152-4°,  $d_{18}$  0.8982,  $n_D^{21}$  1.4375. Reaction of 34 g.  $Et_3SiOH$  with 4 g. Na, followed by 6.8 g.  $PCl_3$  gave 9.3 g.  $(Et_3SiO)_3P$ ,  $b_3$  164-6°,  $d_{18}$  0.9308,  $n_D^{21}$  1.4518. The use of  $POCl_3$  similarly gave  $(Et_3SiO)_3PO$ ,  $b_3$  181-3°,  $d_4^{20.5}$  0.9658,  $n_D^{21}$  1.4460.

*Organophosphorus*

**Application of Hammett equation to the theory of tautomeric equilibrium.  
Thiono-thiole tautomerism of thiophosphoric compounds.**

M.I. Kabachnik, T.A. Mastryukova, A.B. Shipov and T.A. M. lent'eva (Inst. Hetero-Org. Compds., Moscow). Doklady Akad. Nauk SSSR, 124, 1061-64 (1959).  
Cf. this j. 83, 407, 859 (1952); Uspekhi Khim. 25, 137 (1956); Zhur. Obshchei Khim. 25, 684 (1955); this j. 104, 861 (1955); 110, 395 (1956); 83, 859 (1952).

The ionization constants of 2 tautomeric forms of a substance may be expressed through the Hammett equation form of  $pK = pK^0 - \rho \Sigma \sigma$ , for each form. Since the actual exptl. detn. of  $pK$  ~~xxxxxxxxxxxxxxxxxxxxxxxxxxxx~~ gives only some effective constants  $K_a$ , rather than the constants of the individual forms, it is possible to derive the formula  $K_T = 10^a - 1$ , where  $a$  is the deviation (on ordinate axis) of the exptl.  $pK$  curve from the asymptote which coincides with the straight line  $pK_1 = pK_1^0 - \rho \Sigma \sigma$ , and  $pK_a = pK_1 - \log(K_T + 1)$ , where  $pK_a$  is the result of an exptl. detn. of the ionization constant of a tautomer system and  $pK_1$  is that of one of the tautomeric forms and  $K_T$  is the tautomerism equil. constant. This equation permits an exptl. soln. of tautomeric equil. problems, as follows. The apparent ionization constants are detd. by some method for a series of substances of one class, differing only by the nature of substituents, and the data are used to construct a plot of  $pK$  vs.  $\Sigma \sigma$ . If the plot is a straight line, the tautomeric equil. is shifted almost totally to one tautomer. If the plot is a curve, part of which fits the rectilinear form and the remainder curves away from the latter, this shows a displacement of the equil. toward one of the forms, and the deviation  $a$ , cited above, measured on the plot, affords a detn. of the tautomeric equil. constant  $K_T$ . In the present paper this principle was applied to a series of P-S acid derivs. with the indicated amount of the thiole form (in %) being estd.:  $(PhO)_2PSON$ , m. 86-87°, 80% in 7% EtOH, 79% in 80% EtOH;  $(MeO)_2PSON$ , (Na salt with m. 156° was used), 74% in 7% EtOH, 68% in 80% EtOH;  $(EtO)_2PSON$ , b<sub>2.5</sub>

106-107°,  $n_D^{20}$  1.4719,  $d_{20}$  1.1806, 54% and 46%; (iso-PrO)<sub>2</sub>PSOH,  $b_{1.5}$  89-90°, 1.4592, 1.0906, 54% and 29%; (p-ClC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PSOH, m. 103-104°, 54% and 28%; (iso-BuO)<sub>2</sub>PSOH,  $b_{0.05}$  83.5-84°, 1.4570, 1.0386, 52% and 27%; (PrO)<sub>2</sub>PSOH,  $b_{0.09}$  108.5-9.5°, 1.4678, 1.1023, 50% and 24%; (BuO)<sub>2</sub>PSOH,  $b_{0.08}$  88-9°, 1.4654, 1.0672, 38% and 11%; MeP(OEt)OSH,  $b_1$  72.5°, 1.4927, 1.1800, 19% and 2%; PhP(OPh)OSH, m. 141-42°, 18% and 2%; MeP(OCH<sub>2</sub>CHMe<sub>2</sub>)OSH,  $b_{0.8}$  112-2.5°, 1.4819, 1.0824, 16% and 1%; MeP(OPr)OSH,  $b_{2.5}$  106-7°, 1.4883, 1.1293, 15% and 1%; EtP(OEt)OSH,  $b_2$  84.5-5.5°, 1.4916, 1.1337, 14% and 1%; MeP(OBu)OSH,  $b_{0.5}$  90°, 1.4891, 1.0998, 12% and 0.8%; PrP(OEt)OSH,  $b_2$  101-102°, 1.4875, 1.0974, 12% and 0.8%; EtP(OEt)OSH,  $b_{0.015}$  64.5-65°, 1.4831, 1.0721, 10% and 0.6%; EtP(OBu)OSH,  $b_1$  110°, 1.4873, 1.0910, 9% and 0.4%; iso-BuP(OBu)OSH,  $b_{0.1}$  82°, 1.4821, 1.0321, 5% and 0.2%; Et<sub>2</sub>PSOH,  $b_{1.5}$  83.5-89°, 1.5262, 1.10-90, 1% and 0.1%; Pr<sub>2</sub>PSOH,  $b_2$  98.5-99°, --, 1% and 0%; iso-Bu<sub>2</sub>PSOH,  $b_{0.25}$  81-1.5°, --, 0.8% and 0%; iso-Pr<sub>2</sub>PSOH, m. 69.5-70.5°, 0.5%, 0%; (MeEtCH)<sub>2</sub>PSOH, m. 102-102.5°, 0.4% and 0%; (Me<sub>3</sub>C)<sub>2</sub>PSOH, m. 144-45°, 0% and 0%. The pK detns. were made potentiometrically with partially neutralized solns. in the alc. concns. indicated above. The equil. constants found fit the Hammett equation satisfactorily. Thus the deviation of pK values from the rectilinear dependence of pK<sub>a</sub> on  $\sigma$  may be used for estn. of the tautomeric equil. position.

*a* *Organophosphorus*

A method of synthesis of acid esters of phosphinic acids.

M. I. Kabachnik, E. N. Tsvetkov and Chshan Zhun Yui (Inst. Metere-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 125, 1260-2 (1959).

Cf. Arbusev et al. Invest. Akad. Nauk S.S.R., Otdel. Khim. Nauk 1952, 956. Also of. Kabachnik et al. this j. 117, 817 (1957).

The previously described reaction of prepn. of ~~XXXXXXXXXXXXXXXXXXXX~~  $RP(OR)_2$  from  $(RO)_2PCl$  and  $RMgX$  was extended to the conversion of the former by direct hydrolysis to  $ROP(O)NR$ . Thus, addn. of 0.11 mole  $RMgX$  in  $Et_2O$  dropwise to 0.1 mole  $(RO)_2PCl$  in 50 ml.  $Et_2O$  and  $-60^\circ$ , followed by warming to  $20^\circ$ , addn. of 50 ml. of 5%  $NH_4Cl$  soln., standing overnight, extn. of the aq. layer with  $CHCl_3$ , drying the combined org. layers and distn. (all operations done under  $N_2$ ) gave the desired  $RP(O)(OR')N$  (R and R' shown, resp.): Me, Bu, 55.1%,  $b_2$  47-8°,  $n_D^{20}$  1.4321,  $d_{20}$  0.9959; Et, Bu, 53%,  $b_{10}$  94-5°, 1.4350, 0.9769; Pr, Bu, 60%,  $b_2$  67-7.5°, 1.4347, 0.9635; iso-Pr, Bu, 59.1%,  $b_{2.5}$  58.5-60.2°, 1.4321, 0.9581; Bu, Et, 54.6%,  $b_{1.5}$  49-9.5°, 1.4350, 0.9834; iso-Bu, Et, 54%,  $b_6$  76-7°, 1.4310, 0.9730; Ph, Bu, 58.1%,  $b_1$  99.2-100°, 1.5144, 1.0758;  $PhCH_2$ , Bu, 58.4%,  $b_2$  113-15.2°, 1.5160, 1.0646.  $PhCH_2P(O)(OBu)N$  treated with Na in MePh gave the Na salt which with  $PhCH_2Cl$  after reflux of 3 hrs. gave  $(PhCH_2)_2P(O)OBu$ , 67%, m. 77.5-8° (from petr. ether), which boiled 10 hrs. with KOH soln. gave  $(PhCH_2)_2PO_2H$ , m. 191.5-2.3°. Similarly  $PrP(O)(OBu)N$  gave 58.7%  $Pr_2P(O)OBu$ ,  $b_{2.5}$  90.5-1.5°, 1.4419, 0.9389.



*Organic insectofungicides*

**Organic insectofungicides. XII. Reaction of dialkyl phosphochlorothioates and thiophosphoryl chloride with phenols in the presence of tertiary amines.**  
 Ya. A. Mandel'baum, N. N. Mel'nikov and Z. M. Bakanova (Fertil. and Insectofungic. Inst., Moscow). Zhur. Obshchei Khim. 29, 1149-51 (1959). cf. Uspekhi Khim. 22, 253 (1953).

To 0.1 mole ArOH and 0.105 mole  $\text{Et}_3\text{N}$  in PhBr, PhCl,  $\text{Na}_2\text{CO}_3$  or MeOH, EtOH or iso-PrOH (the latter is best for nitro deriva.) there was added at 10-14° 0.1 mole  $(\text{RO})_2\text{PSCl}$ ; after 3 hrs. the mixt. was treated with  $\text{H}_2\text{O}$ , and the product was washed with aq.  $\text{Na}_2\text{CO}_3$  and distd. Thus were prepd.: 77.5%  $(\text{MeO})_2\text{PSOC}_6\text{H}_4\text{NO}_2\text{-p}$ ,  $b_2$  158°, m. 36°; 80%  $(\text{MeO})(\text{EtO})\text{PSOC}_6\text{H}_4\text{NO}_2\text{-p}$ ,  $b_{0.15}$  120-1°,  $d_{20}$  1.3182,  $n_D^{20}$  1.5470; 82%  $(\text{EtO})_2\text{PSOC}_6\text{H}_4\text{NO}_2\text{-p}$ ,  $b_{0.04}$  115°, 1.2655, 1.5385; 60%  $(\text{EtO})_2\text{PSOPh}$ ,  $b_{0.1}$  117-22°, 1.1763, 1.5110; 47%  $(\text{EtO})_2\text{PSOC}_6\text{H}_3\text{-Cl}_2\text{-o,p}$ ,  $b_{0.3}$  150-4°, 1.3083, 1.5235. Addn. of 0.1 mole ArOH and 0.1 mole  $\text{Et}_3\text{N}$  in 40 ml.  $\text{C}_6\text{H}_6$  at 10-20° to 0.2 mole  $\text{PSCl}_2$  in 50 ml.  $\text{C}_6\text{H}_6$ , followed by filtration and washing with  $\text{H}_2\text{O}$  gave: 43%  $\text{PhOPSCl}_2$ ,  $b_{15}$  129°, 1.4050, 1.5730, and 53%  $\text{p-O}_2\text{NC}_6\text{H}_4\text{OPSCl}_2$ ,  $b_{0.15}$  130-5°, m. 54°.



Synthesis of organophosphorus compounds from hydrocarbons and their derivatives. IX. Oxidative chlorophosphonation of 1-butene, 2-butene and cyclohexene. Yu. M. Zinov'ev and L. Z. Soberovskii. Zhur. Obshchei Khim. 29, 615-9(1959). Passage of  $O_2$  and 1-butene into  $PCl_3$  gave a range of products  $RClPOCl_2$ , which on fractionation gave (percentages refer to phosphonic dichloride obtained): 26.8% mixed  $EtCNCICH_2POCl_2$  and  $EtCH(CH_2Cl)POCl_2$ ,  $b_2$  85-6°,  $d_{20}$  1.3925,  $n_D^{20}$  1.4925, and 73.2%  $MeCHClCHMePOCl_2$ ,  $b_2$  73-4°, 1.3950, 1.4857. 2-Butene gave 100%  $MeCHClCHMePOCl_2$ ,  $b_2$  70-4°, 1.3831, 1.4820. BuCl gave 9.5%  $PrCNCIPCl_2$ ,  $b_2$  78-9°, 1.3779, 1.4886, 20.5%  $EtCH(CH_2Cl)POCl_2$ ,  $b_2$  84-5°, 1.3948, 1.4946, 54%  $MeCH(POCl_2)CH_2CH_2Cl$ ,  $b_2$  95-8°, 1.4028, 1.4963, and 16%  $ClCH_2(CH_2)_3POCl_2$ ,  $b_2$  110-3°, 1.3952, 1.4950. 2-Chlorobutane gave mixed isomers  $C_4H_8ClPOCl_2$ ,  $b_{2.5}$  85-93°, 1.3903, 1.4905. Contrary to Isbell et al. (JACS 78, 6042(1956)), passage of  $O_2$  into 41 g. cyclohexene and 455 g.  $PCl_3$  at 20° gave 40.4% crude product,  $b_2$  120-35°. Fractionation of this gave a high boiling fraction of

c *Organophosphorus*

**Organic insectofungicides. XXXVIII. Reaction of thiophosphoryl chloride and alkyl dichlorophosphorothioates with alcohols.**

N. N. Mel'nikov, Ya. A. Mandel'baum and P. G. Zaks (Fertilizer and Insecticide Res. Inst., Moscow). Zhur. Obshchei Khim. 29, 522-6 (1959).

Cf. this j. 37, 1908 (1957).

To 1 mole  $\text{PSCl}_3$ , there was added with stirring and cooling to 15-20° 10 moles MeOH and after stirring 3 hrs., the mixt. was washed with  $\text{H}_2\text{O}$  and the residue yielded 53%  $(\text{MeO})_2\text{PSCl}$ ,  $b_{16}$  65-6°,  $d_{20}^{20}$  1.3351,  $n_D^{25}$  1.4834; similarly 60 moles EtOH in 24 hrs. gave 34%  $(\text{EtO})_2\text{PSCl}$ ; 60 moles PrOH gave in 27 hrs. 46%  $(\text{PrO})_2\text{PSCl}$ , and 60 moles BuOH gave in 29 hrs. 48%  $(\text{BuO})_2\text{PSCl}$ . The excess ROH was either washed out with  $\text{H}_2\text{O}$  or distd. in vacuo. Similar reaction but requiring longer stirring was used to prepare  $(\text{RO})_3\text{PS}$ , but only the reaction with MeOH gave the desired results. Thus, 60 moles MeOH and 1 mole  $\text{PSCl}_3$  in 48 hrs. at 20° gave 6%  $(\text{MeO})_3\text{PS}$ ,  $b_{13}$  72-4°, 1.2192, 1.4599. Similarly 10 moles of MeOH and 1 mole  $\text{MeOPSCl}_2$  in 6 hrs. at 5-10° gave 71%  $(\text{MeO})_2\text{PSCl}$ ,  $b_{10}$  56-7°,  $d_{20}^{20}$  1.3351,  $n_D^{25}$  1.4834; 40 moles EtOH and 1 mole  $\text{EtOPSCl}_2$  gave in 24 hrs. at 20-30° 61%  $(\text{EtO})_2\text{PSCl}$ ; similarly was prepd. 63%  $(\text{PrO})_2\text{PSCl}$ ,  $b_{17}$  109-11°, 1.1648, 1.4650, and 60%  $(\text{BuO})_2\text{PSCl}$ ,  $b_{15}$  140-2°, 1.0695, 1.4601. Reaction of various  $\text{ROPSCl}_2$  with MeOH (10-15 moles) gave in 1.5-4 hrs. at 20-30° the following mixed products: 81%  $(\text{MeO})(\text{EtO})\text{PSCl}$ ,  $b_{17}$  80-1°,  $d_{20}$  1.2506, 1.4740; 65%  $(\text{MeO})(\text{PrO})\text{PSCl}$ ,  $b_{25}$  107-10°, 1.1852, 1.4650; 77%  $(\text{MeO})(\text{BuO})\text{PSCl}$ ,  $b_{0.3}$  45-7°, 1.1830, 1.4765; 90%  $(\text{MeO})(\text{iso-BuO})\text{PSCl}$ ,  $b_{22}$  110-4°, 1.1364, 1.4600; 92%  $(\text{MeO})(\text{iso-AmO})\text{PSCl}$ ,  $b_{32}$  138-40°, 1.1261, 1.4672. Similarly 40 moles MeOH and 1 mole  $\text{MeOPSCl}_2$  in 26 hrs. at 20° gave 32%  $(\text{MeO})_3\text{PS}$ , while 20 moles MeOH and 1 mole  $(\text{MeO})_2\text{PSCl}$  in 24 hrs. at 20° gave a 56% yield of  $(\text{MeO})_3\text{PS}$ . Similarly 20 moles ROH and  $(\text{MeO})_2\text{PSCl}$  in 24 hrs. at 20-30° gave: 46%  $(\text{MeO})_2\text{PS}(\text{OEt})$ ,  $b_{25}$  96°,  $d_{20}$  1.1507,  $n_D^{20}$  1.4520; 73%  $(\text{MeO})_2\text{PS}(\text{OPr})$ ,  $b_{22}$  104-5°, 1.1203, 1.4571; and 30%  $(\text{MeO})_2\text{PS}(\text{OBu})$ ,  $b_{20}$  114°, 1.0941, 1.4560. Thus,  $\text{PSCl}_3$  and  $\text{ROPSCl}_2$  react like other polyfunctional acid chlorides and their reaction with ROH is not limited to but one substitution stage.

a Organophosphorus

Difluorochloromethane as a difluoromethylating agent. II. Reaction of difluorochloromethane with dialkyl sodiophosphites.

L. Z. Soborovskii and N. F. Baiba. Zhur. Obshchei Khim. 29, 1144-6 (1959).  
 Passage of 52 g.  $\text{CHClF}_2$  at  $30-5^\circ$  into a soln. of 11.5 g. Na and 69 g.  $(\text{EtO})_2\text{PHO}$  in petr. ether gave a ppt. of NaCl and on the following day the filtered soln. gave 48.6%  $\text{CHF}_2\text{PO}(\text{OEt})_2$ ,  $b_{12}$   $85.6-8.5^\circ$ ,  $d_{20}$  1.1934. Similarly were prepd: 48.5% di-iso-Pr ester,  $b_{12}$   $89-90^\circ$ ,  $d_{20}$  1.1153,  $n_D^{20}$  1.3870; 67.3% di-Bu ester,  $b_{12}$   $124-5^\circ$ , 1.0913, 1.4084 ( in this case the pptn. of NaCl occurred only after the addn. of a little  $\text{H}_2\text{O}$  ). The latter ( 18 g. ) was treated gradually with 25 g.  $\text{PCl}_5$  at  $70^\circ$ , yielding 11.3 g. mixed  $\text{BuCl}$  and  $\text{PCl}_3$ ,  $\text{POCl}_3$  and 3 g.  $\text{CHF}_2\text{POCl}_2$ ,  $b_{50}$   $50-2^\circ$ ; some 50% of the mixt. was an undistillable mass. If this reaction is run with equimolar proportion of  $\text{PCl}_5$  the C-P bond is ruptured and the main product is  $\text{BuOPOCl}_2$ ,  $b_{17}$   $89^\circ$ . Reaction of  $\text{PCl}_5$  with  $\text{CHF}_2\text{PO}(\text{OEt})_2$  similarly gave  $\text{EtOPOCl}_2$  and only a trace of  $\text{CHF}_2\text{POCl}_2$ . Reaction of  $\text{CHClF}_2$  with  $(\text{MeO})_2\text{POMe}$  gave only a trace of  $\text{CHF}_2\text{PO}(\text{OMe})_2$  and much  $(\text{MeO})_2\text{PHO}$  if the reaction is run in ROH; this reaction course is ascribed to facile formation of  $\text{MeOCHF}_2$  and the removal of MeONa component of the equil. mixt. of  $\text{MeONa}-(\text{MeO})_2\text{PHO}$ .

4

$C_6H_{10}ClPOCl_2$ ,  $b_3$  127-30°, 1.4162, 1.5287, and a low boiling fraction (crude)  
 $b_4$  118-24°, which distd. from activated C to eliminate residual HCl, gave  
 $C_6H_9POCl_2$ ,  $b_2$  99-102°, 1.3520, 1.5250.

Synthesis of organophosphorus compounds from hydrocarbons and their derivatives. X. Oxidative chlorophosphonation of some ethylene derivatives. L. Z. Soborovskii, Yu. M. Zinov'ev and T. G. Spiridenova. Zhur. Obshchei Khim. 29, 1139-41 (1959). cf. Doklady Akad. Nauk SSSR 109, 98 (1956) and this j. 28, 1870 (1958).

Passage of  $O_2$  at  $0^\circ$  into 20 g.  $(:CHCl)_2$  and 400 g.  $PCl_3$  gave 18.8 g. (40%)  $Cl_2CHCHClPOCl_2$ ,  $b_3$  89-92°,  $d_{20}$  1.7172,  $n_D^{20}$  1.4990, which is slowly attacked by  $H_2O$ . Passage of  $O_2$  into 34 g.  $CH_2:CHBr$  and 400 g.  $PCl_3$  gave 24.2 g. (29%) material,  $b_{0.05}$  95-125°, which on further fractionation gave 8 g.  $BrCH:CH-POCl_2$ ,  $b_3$  81-2°, 1.7415, 1.4839, and 3.7 g.  $BrCH_2CHClPOCl_2$ ,  $b_3$  99-100°, 1.9720, 1.5378. Passage of 15 l. dry  $CH_2:CHF$  at  $-70^\circ$  into 275 g.  $PCl_3$  and percolation of  $O_2$  at  $-70^\circ$  until the mass crystallized gave 6.3% (7.6 g.)  $C_2H_5PClPOCl_2$ ,  $b_{30}$  109°, 1.6531, 1.4715. Passage of  $O_2$  into 16 g.  $CHF:CHCl$  and 300 g.  $PCl_3$  at  $-5^\circ$  gave 11.7 g. (25.2%)  $C_2H_2PCl_2POCl_2$ ,  $b_3$  66-70°, 1.6893, 1.4640. Passage of  $O_2$  at 20-5° into 60 g.  $CH_2:CHSO_2F$  and 400 g.  $PCl_3$  gave 13.5 g. (9.3%)  $FSO_2CH_2CH_2ClPOCl_2$ ,  $b_3$  95-7°, 1.7264, 1.4618. Similar reactions attempted with vinylidene chloride, trichloroethylene and tetrachloroethylene either gave a polymer or failed to proceed (last 2). Passage of  $Cl_2$  at  $0-5^\circ$  into  $CH_2:CHBr$  in  $CCl_4$  gave 52%  $BrClCHCH_2Cl$ ,  $b_{750}$  134-5°, 1.8662, 1.5136.

**Vinyl esters of phosphorous acid.**

A.N.Nesmeyanov, I.F.Lutsenko, Z.S.Kraits and A.P.Bekovoi (M.V.Lomonosov State Univ., Moscow). Doklady Akad.Nauk SSSR, 184, 1251-54 (1959).

Cf. Nesmeyanov et al. Izvest.Akad.Nauk SSSR, etdel.khim.nauk 1949, 601.

To 0.1 mole  $\text{Hg}(\text{CH}_2\text{CHO})_2$  and 0.1 mole  $\text{Et}_3\text{N}$  in 250 ml. isopentane was added over 1 hr. with vigorous stirring 0.1 mole  $(\text{EtO})_2\text{PCl}$  in 50 ml. isopentane, after which 0.1 mole  $\text{Hg}(\text{CH}_2\text{CHO})_2$  and 0.1 mole  $\text{Et}_3\text{N}$  was added, followed by 0.1 mole  $(\text{EtO})_2\text{PCl}$  and the whole was then stirred 1 hr. longer. The liquid portion was sepd. and distd. yielding 63%  $(\text{EtO})_2\text{POCH:CH}_2$ ,  $b_{28}$  58-59°,  $n_D^{20}$  1.4258,  $d_{20}$  0.9787. While the same product also forms from  $\text{ClHgCH}_2\text{CHO}$ , the yields are very low and the product difficult to purify. The following were prepd. similarly, except that the Me ester required the use of  $\text{PhNEt}_2$  in place of  $\text{Et}_3\text{N}$ .  $(\text{MeO})_2\text{POCH:CH}_2$ , 46%,  $b_{80}$  55-56°, 1.4255, 1.0406;  $(\text{PrO})_2\text{POCH:CH}_2$ , 62%,  $b_3$  53-54°, 1.4322, 0.9518;  $(\text{BuO})_2\text{POCH:CH}_2$ , 70%,  $b_4$  55-56°, 1.4360, 0.9361;  $(\text{PhO})_2\text{POCH:CH}_2$ , 56%,  $b_3$  143-44°, 1.5575, 1.1567. To 250 ml. isopentane there was added over 3 hrs. in 4 equal portions 135 g.  $\text{Hg}(\text{CH}_2\text{CHO})_2$ , 45.5 g.  $\text{Et}_3\text{N}$  and 20.5 g.  $\text{PCl}_3$ ; after stirring 1 hr. there was formed 46%  $\text{P}(\text{OCH:CH}_2)_3$ ,  $b_{30}$  51-52°, 1.4485, 1.0262. To 0.1 mole  $\text{Hg}(\text{CH}_2\text{CHO})_2$  and 0.1 mole  $\text{Et}_3\text{N}$  in 250 ml. isopentane there was added over 1 hr. 0.05 mole  $\text{EtOPCl}_2$  in 25 ml. isopentane; over 4 hrs. there was then added 120 g.  $\text{Hg}(\text{CH}_2\text{CHO})_2$ , 40.4 g.  $\text{Et}_3\text{N}$  and 29.4 g.  $\text{EtOPCl}_2$  after which the mixt. was stirred 1 hr. and yielded after usual treatment 60%  $\text{EtOP}(\text{OCH:CH}_2)_2$ ,  $b_{30}$  57-58°, 1.4380, 1.0015; similarly were prepd.: 60%  $\text{MeOP}(\text{OCH:CH}_2)_2$ ,  $b_{60}$  60-61°, 1.4390, 1.0368; 60%  $\text{PrOP}(\text{OCH:CH}_2)_2$ ,  $b_{11}$  56-57°, 1.4392, 0.9908; 55%  $\text{BuOP}(\text{OCH:CH}_2)_2$ ,  $b_7$  63°, 1.4412, 0.9873; 79%  $\text{PhOP}(\text{OCH:CH}_2)_2$ ,  $b_{10}$  108-109°, 1.5151, 1.1037. The divinyl esters tended to polymerize during distn. and only by addn. of an equivalent amount of the base was it possible to



suppress this tendency. The vinyl esters are readily hydrolyzed with  $H_2O$  with evolution of heat. Addn. of  $SO_2$ -fuchsin, immediately gave the characteristic color test. The trivinyl ester is hydrolyzed rapidly by even just traces of moisture, forming a gelatinous mass which heats up rapidly and darkens, evolving AcH. Heating the vinyl esters with S on a steam bath several hrs (6-8) gave the following thiophosphates:  $(EtO)_2P(S)OCH:CH_2$ , 88%,  $b_{7.5}$  83°, 1.4562, 1.0904;  $(PrO)_2P(S)OCH:CH_2$ , 84%,  $b_8$  97°, 1.4581, 1.0805;  $(BuO)_2P(S)OCH:CH_2$ , 68%,  $b_8$  126-27°, 1.4575, 1.0195;  $(PhO)_2P(S)OCH:CH_2$ , 50%,  $b_2$  163-64°, 1.5655, 1.2164;  $EtOP(S)(OCH:CH_2)_2$ , 62%,  $b_7$  72-73°, 1.4634, 1.1017;  $BuOP(S)(OCH:CH_2)_2$ , 65%,  $b_9$  96°, 1.4654, 1.0617; 74%  $PhOP(S)(OCH:CH_2)_2$ ,  $b_{10}$  134-35°, 1.5268, 1.1719. Attempted oxidation by various means of the vinyl phosphites failed to yield the desired vinyl phosphates since polymerization intervened. Preliminary expts. indicate that the Arbuzov isomerization of the vinyl esters is more difficult than in the satd. esters. The addn. of S to Ph and  $Ph_2$  esters requires heating to 130-50°.

*b Organophosphorus*

Phosphorylated chlorovinyl ketones. Preparation of phosphorylated chlorovinyl ketones from vinyl acetate and isopropenyl acetate.

I. P. Lutsenko and M. Kirilov (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 123, 89-91 (1959).

To 125 g.  $\text{PCl}_5$  suspended in  $\text{CCl}_4$  was added over 45 min. 29.5 g.  $\text{CH}_2=\text{CHOAc}$  at  $15-17^\circ$  and after 2 hrs. with gradual heating to  $40^\circ$ , the mixt. was treated with  $\text{SO}_2$  with cooling, and distd. yielding 85%  $\text{Cl}_2\text{CHCHAcPOCl}_2$ ,  $b_2$   $94-5^\circ$ ,  $n_D^{20}$  1.5100,  $d_{20}$  1.5464. This (51.6 g.) in 150 ml.  $\text{Et}_2\text{O}$  was treated over 0.5 hr. with 18.4 g. abs.  $\text{EtOH}$  in 25 ml.  $\text{Et}_2\text{O}$  and after 2 hrs. at  $25-30^\circ$ , the mixt. was air blown 1 hr. and distd. yielding 62.5%  $\text{CHCl}_2\text{CHAcPO}(\text{OEt})_2$ ,  $b_2$   $111-12^\circ$ , 1.4620, 1.2465. If this esterification is run in the presence of pyridine, there is formed a 52% yield of the ester contg. some of the  $\text{CHCl}_2\text{CHAcPO}(\text{OEt})_2^{(I)}$  even after several redistns. Heating the ester with  $\text{Et}_3\text{N}$  in  $\text{C}_6\text{H}_6$  2 hrs. gave 88% I,  $b_2$   $102-3^\circ$ , 1.4645, 1.1861. Similarly 83.2 g.  $\text{PCl}_5$  and 20 g.  $\text{CH}_2=\text{CMeOAc}$  gave 70%  $\text{MeCCl}_2\text{CHAcPOCl}_2$ ,  $b_{1.5}$   $112-13^\circ$ , 1.5233, 1.4413; the  $\text{MeCCl}_2\text{CHAcPOCl}_2$  was unstable and lost  $\text{HCl}$  directly. Reaction of the chloride with  $\text{EtOH}$  in the presence of pyridine gave 75%  $\text{MeCCl}_2\text{CHAcPO}(\text{OEt})_2$ ,  $b_1$   $114-5^\circ$ , 1.4710, 1.1726.

**Ethylenimine derivatives. I. Ethylenimides of phosphoric acid.**

A. A. Krepacheva and V. A. Parshina (B. Ordzhonikidze All Union Chem. Pharm. Res. Inst., Moscow). Zhur. Obshchei Khim. 29, 556-60 (1959). Cf. Bastian, Ann. 566, 210 (1950); US Pat 2,606,900 (C.A. 47, 5423 (1953)); US Pat. 2,654,758 (C.A. 48, 10053(1954)); US Pat. 2,670,347 (C.A. 49, 2481(1955)).

To 14.3 g.  $\text{POCl}_3$  in abs.  $\text{Et}_2\text{O}$  was added at  $0^\circ$  25 g.  $2\text{-C}_{10}\text{H}_7\text{NH}_2$  in  $\text{Et}_2\text{O}$  and after 1 hr. with cooling and 3 hrs. at room temp., there formed after filtration and evapn. 52.8%  $2\text{-C}_{10}\text{H}_7\text{NHPOCl}_2$ , m.  $115\text{-}17^\circ$  (from  $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ ); thus were prepd. also:  $\text{PhNHPOCl}_2$ , 42.7%, m.  $70^\circ$ ;  $p\text{-ClC}_6\text{H}_4\text{NHPOCl}_2$ , 74%, m.  $103\text{-}4^\circ$ ;  $p\text{-IC}_6\text{H}_4\text{NHPOCl}_2$ , 48%, m.  $105\text{-}7^\circ$ ;  $m\text{-O}_2\text{NC}_6\text{H}_4\text{NHPOCl}_2$ , 66.8%, m.  $85\text{-}6^\circ$ ;  $p\text{-MeOC}_6\text{H}_4\text{NHPOCl}_2$ , 41.3%, m.  $71\text{-}2^\circ$ ;  $p\text{-EtO}_2\text{CC}_6\text{H}_4\text{NHPOCl}_2$ , 68.8%, m.  $100\text{-}2^\circ$ ;  $m\text{-ClC}(\text{O})\text{C}_6\text{H}_4\text{NHPOCl}_2$ , 43%, m.  $110.5\text{-}11.5^\circ$ ;  $2,4\text{-(Cl}_2\text{PONH)}_2\text{MeC}_6\text{H}_3$ , 53.5%, m.  $153\text{-}4^\circ$ . The above products were best prepd. by refluxing  $\text{POCl}_3$  with HCl salt of the amine. Addn. at  $6^\circ$  of 8.39 g.  $\text{PhNHPOCl}_2$  in  $\text{C}_6\text{H}_6$  to 3.44 g. ethylenimine and 8.08 g.  $\text{Et}_3\text{N}$  in  $\text{C}_6\text{H}_6$ , stirring 4 hrs. at room temp. and setting the mixt. aside until the next day gave after filtration and evapn. 5%  $\text{PhNHPO}(\text{NCH}_2\text{CH}_2)_2$ , m.  $143\text{-}4^\circ$ . Similarly were prepd.: 27%  $p\text{-ClC}_6\text{H}_4\text{NH}$  analog, m.  $170\text{-}1.5^\circ$ ; 77%  $p\text{-IC}_6\text{H}_4\text{NH}$  analog, m.  $176\text{-}7^\circ$ ; 57%  $m\text{-O}_2\text{NC}_6\text{H}_4\text{NH}$  analog, m.  $166\text{-}7^\circ$ ; 54.5%  $p\text{-MeOC}_6\text{H}_4\text{NH}$  analog, m.  $102\text{-}3^\circ$ ; 71.7%  $p\text{-EtO}_2\text{CC}_6\text{H}_4\text{NH}$  analog, m.  $151\text{-}2^\circ$ ;  $m\text{-(CH}_2\text{CH}_2\text{NCO)C}_6\text{H}_4\text{NH}$  analog

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82%, m. 131-2.5°; 38% 2-C<sub>10</sub>H<sub>7</sub>NH analog, m. 148°; 55.9% 2,4-(CH<sub>2</sub>CH<sub>2</sub>NPOHN)<sub>2</sub>Me-C<sub>6</sub>H<sub>3</sub>, m. 205-6°. To 1.72 g. ethylenimine, 4.04 g. Et<sub>3</sub>N and 20 ml. C<sub>6</sub>H<sub>6</sub> was added at 6° 4.22 g. PhOP(=O)Cl<sub>2</sub> in 15 ml. C<sub>6</sub>H<sub>6</sub>; after 4-5 hrs. stirring and allowing to warm up overnight, the filtered and evapd. soln. gave 80% PhOP(=O)(NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>, m. 58-9°; similarly was prepd. 64% p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>O analog, m. 73.5-74°. The deriv. based on m-aminebenzoic acid was verified as to the above structure as an ethylenimide by means of infrared spectrum, which showed the 1673 cm<sup>-1</sup> band typical of carbenamide structures.

*Organophosphorus*

Chlorides of esters of phosphonocarboxylic acids. I. Synthesis of P-mono-chlorides of dialkyl esters of phosphonocarboxylic acids.

K. A. Petrov, F. L. Maklyaev and M. A. Korshunov (Milit. Acad. Chem. Defence). Zhur. Obshchei Khim. 29, 301-5 (1959).

Gradual addn. of 0.21 mole powd.  $\text{PCl}_5$  to 0.2 mole  $(\text{RO})_2\text{P}(\text{O})(\text{CH}_2)_x\text{CO}_2\text{R}$ , and stirring 15-30 min. at  $18^\circ$  and 20-40 min. at  $30-50^\circ$ , followed by decompn. of unreacted  $\text{PCl}_5$  with  $\text{SO}_2$  at  $18^\circ$  gave the following products when the reaction is run in 1 vol. dry  $\text{CCl}_4$ : 63%  $(\text{MeO})\text{ClP}(\text{O})\text{CO}_2\text{Me}$ ,  $b_1$   $85-6^\circ$ ,  $d_{20}$  1.4167,  $n_D^{20}$  1.4475; 82%  $(\text{EtO})\text{ClP}(\text{O})\text{CO}_2\text{Et}$ ,  $b_5$   $107-8^\circ$ , 1.2410, 1.4385; 81%  $(\text{BuO})\text{ClP}(\text{O})\text{CO}_2\text{Et}$ ,  $b_{0.35}$   $98-101^\circ$ , 1.1977, 1.4387; 56%  $(\text{BuO})\text{ClP}(\text{O})\text{CO}_2\text{Bu}$ ,  $b_{3-4}$   $133-4^\circ$ , 1.1326, 1.4455; 84%  $(\text{EtO})\text{ClP}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_3$   $110-11^\circ$ , 1.2584, 1.4476; 58%  $(\text{iso-PrO})\text{ClP}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.25}$   $92-3^\circ$ , 1.1947, 1.4430; 63%  $(\text{iso-AmO})\text{ClP}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.03}$   $110-12^\circ$ , 1.1384, 1.4463; 68%  $(\text{BuO})\text{ClP}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.35}$   $120-22^\circ$ , 1.1551, 1.4440; 80%  $(\text{MeO})\text{ClP}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ,  $b_{0.2}$   $92-4^\circ$ , 1.3306, 1.4506; 81%  $(\text{EtO})\text{ClP}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.1}$   $101-2^\circ$ , 1.2502, 1.4555; 80%  $(\text{iso-Pr})\text{ClP}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.05}$   $113-16^\circ$ , 1.2352, 1.4486; 74%  $(\text{BuO})\text{ClP}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.0}$   $128-33^\circ$ , 1.1526, 1.4520; 78%  $(\text{EtO})\text{ClP}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_1$   $118-9^\circ$ , 1.2207, 1.4621. Treatment of the appropriate chloride ( 2 g.) in  $\text{C}_6\text{H}_6$  with cooling with 88 ml. soln. of  $\text{NH}_3$  in  $\text{C}_6\text{H}_6$  and keeping the mixt. 24 hrs. in closed flask gave after filtration and evapn. 0.78 g.  $(\text{EtO})\text{H}_2\text{NP}(\text{O})\text{CO}_2\text{Et}$ , m.  $137^\circ$  ( from  $\text{EtOH}-\text{C}_6\text{H}_6$  ). Similarly was prepd.  $\text{H}_2\text{N}(\text{EtO})\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$ , m.  $103^\circ$  ( from  $\text{C}_6\text{H}_6$ -petr. ether). Passage of  $\text{Cl}_2$  at  $5^\circ$  into 31 g.  $(\text{MeO})_2\text{P}(\text{O})\text{CO}_2\text{Me}$  in 100 ml.  $\text{CCl}_4$  in 25.4 g.  $\text{BCl}_3$  with ice/salt cooling 30 min., followed by heating to  $40^\circ$  ( $\text{PCl}_5$  ppt. dissolved ) and the chlorination was repeated until all  $\text{P}^{\text{III}}$  had reacted ( 3 hrs.); distn. gave  $(\text{MeO})\text{ClP}(\text{O})\text{CO}_2\text{Me}$ , identical with the above in 63% yield. Similar chlorination of 32.1 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$  and 21 g.  $\text{PCl}_3$  gave 70% corresponding monochloride, which decomposes at above  $180^\circ$ , as does the phosphonoformic deriv. above. Similarly was prepd. 56.6%  $(\text{BuO})\text{ClP}(\text{O})\text{CH}_2\text{Bu}$ , which decomp. above  $190^\circ$ . Heating 5 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$  and 7.95 g.  $\text{SOCl}_2$  9 hrs. at  $80-90^\circ$  gave 33% corresponding monochloride; similar was prepd. 42%  $(\text{MeO})\text{ClP}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ .  $(\text{EtO})\text{ClP}(\text{O})(\text{CH}_2)_2\text{CO}_2\text{Et}$ ,  $b_2$   $123-5^\circ$ .

X

*Organophosphorus*

**Chlorides of esters of phosphonocarboxylic acids. II. Dichlorides of C-alkyl esters of phosphonocarboxylic acids.**

K. A. Petrov, F. L. Maklyasv and M. A. Korshunov. Zhur. Obshchei Khim. 29, 585-8 (1959); cf. 29, 301 (1959).

$(RO)_2P(O)(CH_2)_nCO_2R$  react with excess  $PCl_5$  to yield the corresponding P,P-dichlorides, with the carballoxy group not being affected even with large amt. of  $PCl_5$  at  $120^\circ$ . To 30 g.  $(EtO)_2P(O)CH_2CO_2Et$  was added over 1 hr. 39 g.  $PCl_5$ , the mixt. was heated 1.5 hrs. on a steam bath, then placed in a sealed tube and heated 5 hrs. at  $115-20^\circ$ , after which  $SO_2$  was introduced for 20 min. at room temp. and the residue was distd. yielding 68%  $Cl_2P(O)CH_2CO_2Et$ ,  $b_{0.05} 76-8^\circ$ ,  $d_4^{23} 1.5038$ ,  $n_D^{23} 1.4774$ ; it decomposes above  $135^\circ$  to a brown tar. The above product does not form if the ester in  $PCl_5$  soln. is treated with  $Cl_2$ ; in this case chlorination of the  $CH_2$  group occurs; thus passage of  $Cl_2$  at below  $60^\circ$  ( ice water cooling ) through 100 g. above ester in 184 g.  $PCl_5$  over 9 hrs., chilling to sep.  $PCl_5$ , passage of  $SO_2$  and distn. gave a low b. product and 57.6%  $Cl_2P(O)CCl_2CO_2Et$ ,  $b_8 120-2^\circ$ ,  $d_{20} 1.5603$ ,  $n_D^{20} 1.4920$ . Heating 43 g.  $(EtO)_2P(O)(CH_2)_2CO_2Et$  and 79.5 g.  $PCl_5$  0.5 hr. at  $65^\circ$  and 1 hr. in sealed tube at  $120^\circ$  gave, after  $SO_2$  treatment as above, 85.5%  $Cl_2P(O)(CH_2)_2CO_2Et$ ,  $b_{0.03-0.05} 89-91^\circ$ ,  $d_{20} 1.5602$ ,  $n_D^{20} 1.4640$ .. To 7.1 g. dry HF there was added with icecooling 11.7 g. I; after 50 min. at room temp. and 50 min. at  $50^\circ$ , the residue was treated with 20 ml. dry  $Et_2O$  and 10 g. KF, after which the mass was filtered and distd. yielding  $CNCl_2CO_2Et$  and evidently  $POF_3$ . Addn. of 5 g. I to 4 g. powd.  $KNF_2$  resulted in heat evolution and after 1.5 hrs. at  $100^\circ$  and 2 hrs. at  $140^\circ$  there was isolated some  $CNCl_2CO_2Et$  and low b. material.

*Organophosphorus***Synthesis of acid esters of dialkylaminoalkylphosphonic acids.**

K. A. Petrov, P. L. Maklyaev and N. K. Blisnyuk. Zhur. Obshchei Khim. 29, 588-91 (1959).

Thermal decompn. of HCl salts of esters of dialkylaminoalkylphosphonates yields inner salts of esters, with elimination of an alkyl chloride; the final products are formulated as  $R_2N^+CH_2P(O)(OR)O^-$ . Passage of dry HCl into 20.1 g.  $Me_2NCH_2P(O)(OEt)_2$  in 100 ml. dry  $Et_2O$  at  $-15^\circ$  gave 97.4% crystalline HCl salt, m.  $95^\circ$ ; this (11.8 g.), in  $Et_2O$  was slowly treated with 7.5 g.  $Et_3N$  and after 1 hr. at  $35-40^\circ$ , the ppt. amine salt was sepd. and the filtrate yielded 4.1 g. original free ester, b.  $95^\circ$ . Similarly was prepd. syrupy  $Et_2NCH_2P(O)(OBu)_2 \cdot HCl$  (I); viscous glassy  $Me_2NCH_2P(O)(OEt)_2 \cdot HF$  (this heated to  $130^\circ$  failed to undergo any change). Heating 32 g.  $Et_2NCH_2P(O)(OEt)_2 \cdot HCl$  20 hrs. on a steam bath gave 98%  $EtCl$  and a crystalline residue of 77.8%  $Et_2NCH_2P(O)(OEt)OH$ , m.  $153^\circ$  (from dry  $Me_2CO$ ). Similarly I in 28 hrs. on a steam bath and 22 hrs. at  $130-40^\circ$  gave 97%  $BuCl$  and a syrupy  $Et_2NCH_2P(O)(OBu)OH$  (sol. in  $H_2O$ , forming a neutral soln.). Heating I 20 hrs. on a steam bath gave 97%  $EtCl$  and 97%  $Me_2NCH_2P(O)(OEt)OH$ , m.  $116^\circ$  (from  $Me_2CO$ ).

*d Organophosphorus***Synthesis of aminediphosphonates and aminetriphosphonates.**

K. A. Petrov, P. L. Maklyaev and N. K. Blisnyuk. Zhur. Obshchei Khim. 29, 591-4 (1959).

To 40 g.  $(EtO)_2PNO$  and 4.5 g.  $MeNH_2$  cooled to  $-15^\circ$  was added dropwise 22 g. 40% Formalin (temp. kept below  $20^\circ$ ), the mixt. heated over 0.5 hr. to  $100^\circ$  and kept 15 min. at this temp.; after cooling, 5-10%  $NaOH$  was added, the mixt. extd. with  $C_6H_6$ , the org. layer washed with  $H_2O$  and distd. yielding 60%  $MeN(CH_2P(O)(OEt)_2)_2$ , b.  $149-50^\circ$ ,  $d_{20}$  1.1340,  $n_D^{20}$  1.4470; similarly were prepd.: 54%  $MeN(CH_2P(O)(OCHMe_2)_2)_2$ , b.  $146^\circ$ , 1.0553, 1.4376; and 74.6%  $MeN(CH_2P(O)(OBu)_2)_2$ , b.  $195-7^\circ$ , 1.0320, 1.4480. To 60 g.  $(EtO)_2PNO$  and 19.9 g. 18.6%  $NH_4OH$  was added at  $-10^\circ$  32.6 g. 40% Formalin; treatment as above gave 15.5%  $NH(CH_2P(O)(OEt)_2)_2$ , b.  $150-1^\circ$ , 1.1429, 1.4470 and 19.1%

(I)

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$\text{N}(\text{CH}_2\text{P}(\text{O})(\text{OEt})_2)_3$ ,  $b_{0.8}$  202-4°, 1.1759, 1.4534. Excess phosphite and aldehyde tend to improve the yield of the latter product. Similarly, 50 g.  $(\text{BuO})_2\text{-P}(\text{H})\text{O}$  and 14.1 g. 18.6%  $\text{NH}_4\text{OH}$  with 23.2 g. 40% Formalin gave 21.7%  $\text{NN}(\text{CH}_2\text{-P}(\text{O})(\text{OBu})_2)_2$ ,  $b_{0.6}$  195-6°, 1.0359, 1.4499 and some  $\text{N}(\text{CH}_2\text{P}(\text{O})(\text{OBu})_2)_3$ ,  $b_{0.8}$  240-5°. Heating 6 g.  $\text{NN}(\text{CH}_2\text{P}(\text{O})(\text{OEt})_2)_2$  and 20 ml. 1:1  $\text{HCl}$  in sealed tube 5 hrs. at 140° gave after evapn. a glassy  $\text{NN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , which titrates with  $\text{NaOH}$  as a tribasic acid; tetra-Ag salt, colorless crystals, darkens on heating. Similarly I gave pentabasic  $\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3$ , a glassy solid; hexa-Ag salt, a colorless solid, darkening in light; decomp. on heating. Evidently the free acids exist in the form of zwitterions.



*Org. Chem.*  
~~C~~ Aryloxy-P,P-dimethoxyisophosphazacyls and mixed triaryloxyisophosphazacyl  
 A. V. Kirsanov and G. I. Derkach (Inst. Org. Chem., Acad. Sci., Kiev). Zhur.  
 Obshchei Khim. 29, 600-5 (1959). Cf. this j. 29, 241 (1959).

To 0.01 mole  $\text{RCCl:NPO(OMe)}_2$  in 20 ml.  $\text{C}_6\text{H}_6$  was added 0.0105 mole dry  $\text{ArONa}$  (exothermic) and after stirring until the mixt. became neutral (10-15 min., except for p-nitro deriv. which required 1-2 hrs. refluxing),  $\text{NaCl}$  was removed with  $\text{H}_2\text{O}$ , and the org. layer after evapn. gave  $\text{RC(OR')NPO(OMe)}_2$ :  
 R and R' shown resp.: Ph, p- $\text{ClC}_6\text{H}_4$ , 63.6%, m. 85-7°; Ph, p- $\text{O}_2\text{NC}_6\text{H}_4$ , 30%, m. 131-3°; p- $\text{ClC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 30.6%, m. 112-4°; p- $\text{ClC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , 31.1%, m. 131-3°; p- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 30%, m. 140-2°; p- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , 33.9%, m. 128-30°; m- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 70%, m. 145-7°; m- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , 54.4%, m. 126-8°; 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , p- $\text{ClC}_6\text{H}_4$ , 44.4%, m. 100-3°; 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , 73.4%, m. 151-3°. Similarly were prepd.  $\text{RC(OR')NPO(OPh)}_2$ : 80% Ph, p- $\text{ClC}_6\text{H}_4$ , m. 124-6°; 95.4% Ph, p- $\text{O}_2\text{NC}_6\text{H}_4$ , m. 157-9°; p- $\text{ClC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 100%, m. 143-5°; 81% p- $\text{ClC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , m. 155-7°; p- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 68.8%, m. 118-20°; 55.6% p- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , m. 162-4°; m- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 60.9%, m. 124-6°; 99.9% m- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , m. 128-30°; 79.6% 3,4-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , p-

$\text{ClC}_6\text{H}_4$ , m.  $181-3^\circ$ ; 68.9% 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , m.  $204-6^\circ$ . Refluxing  $\text{RCCl:NPO(OC}_6\text{H}_4\text{Cl-p)}_2$  with dry p- $\text{O}_2\text{NC}_6\text{H}_4\text{ONa}$  in  $\text{C}_6\text{H}_6$  gave  $\text{RC(OC}_6\text{H}_4\text{NO}_2\text{-p)-NPO(OC}_6\text{H}_4\text{Cl-p)}_2$  (R shown): Ph, 85.4%, m.  $142-4^\circ$ ; p- $\text{ClC}_6\text{H}_4$ , 79.2%, m.  $151-3^\circ$ ; p- $\text{O}_2\text{NC}_6\text{H}_4$ , 88.4%, m.  $162-4^\circ$ ; m- $\text{O}_2\text{NC}_6\text{H}_4$ , 85%, m.  $133-5^\circ$ ; 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , 88.77.6%, m.  $209-10^\circ$ . Similarly were prepd.  $\text{RC(OC}_6\text{H}_4\text{Cl-p):NPO(OC}_6\text{H}_4\text{NO}_2\text{-p)}_2$ : Ph, 69.3%, m.  $180-2^\circ$ ; p- $\text{ClC}_6\text{H}_4$ , 73.6%, m.  $139-41^\circ$ ; p- $\text{O}_2\text{NC}_6\text{H}_4$ , 66.9%, m.  $217-9^\circ$ ; m- $\text{O}_2\text{NC}_6\text{H}_4$ , 50.2%, m.  $149-51^\circ$ ; 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , 76.6%, m.  $200-2^\circ$ . The previously described method (cf. above ref.) gave: m- $\text{O}_2\text{NC}_6\text{H}_4\text{CCl:NPO(OC}_6\text{H}_4\text{Cl-p)}_2$ , 80.1%, m.  $120-3^\circ$ ; m- $\text{O}_2\text{NC}_6\text{H}_4\text{CCl:NPO(OC}_6\text{H}_4\text{NO}_2\text{-p)}_2$ , 90%, m.  $130-1^\circ$ ; 79.1% 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_4\text{CCl:NPO(OC}_6\text{H}_4\text{Cl-p)}_2$ , m.  $128-30^\circ$ ; 90% 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{CCl:NPO(OC}_6\text{H}_4\text{NO}_2\text{-p)}_2$ , m.  $55-7^\circ$ . Heating  $\text{RC(OC}_6\text{H}_4\text{NO}_2\text{-p):NPO(OPh)}_2$  with 0.2 N aq. NaOH 1 hr. gave clear solns., which after concn. in vacuo and acidification to Congo red gave 60-70% known  $\text{RCONNPO(OR)}_2$ . Of the products reported here only  $\text{PhC(OC}_6\text{H}_4\text{NO}_2\text{-p):NPO(OMe)}_2$  showed active contact insecticidal properties.

*Originals*

**C-Chloro-P,P-dimethoxy- and C-chloro-P,P-diaryloxyisophosphazonyls.**

G. I. Derkach (Inst. Org. Chem., Acad. Sci., Kiev ). Zhur. Obshchei Khim. 29, 241-5 (1959). Cf. Kirsanov et al. this j. 27, 1080 (1957).

Mixing 0.01 mole  $(\text{MeO})_2\text{P}(\text{O})\text{NHCOR}$  with 0.01 mole  $\text{PCl}_5$  in 10-15 ml. dry  $\text{C}_6\text{H}_6$  or  $\text{PhCl}$  results in an energetic reaction, completed by 5-10 min. at  $60-70^\circ$  and concn. in vacuo gave a residue of  $\text{RCCl:NP}(\text{O})(\text{OR}')_2$  (R, R' shown, resp.)

Ph, Me, 100%, viscous oil; p- $\text{O}_2\text{NC}_6\text{H}_4$ , Me, 100%, m.  $107-10^\circ$ ; m- $\text{O}_2\text{NC}_6\text{H}_4$ , Me, 89.6%, m.  $20-5^\circ$ ; 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , Me, 95.5%, m.  $125-7^\circ$ ; p- $\text{ClC}_6\text{H}_4$ , Me, 99%, liquid. The diphenoxy analogs were prepd. similarly but at  $100-5^\circ$  and were induced to crystallize by rubbing with petr. ether: Ph, Ph, ~~XXXXXX~~ (I) 42.5%, m.  $74-6^\circ$ ; p- $\text{O}_2\text{NC}_6\text{H}_4$ , Ph, 83.5%, m.  $87-9^\circ$ ; m- $\text{O}_2\text{NC}_6\text{H}_4$ , Ph, 81.7%, m.  $127-9^\circ$ ; 3,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3$ , Ph, 61.6%, m.  $115-8^\circ$ ; p- $\text{ClC}_6\text{H}_4$ , Ph, 100%, m.  $55-7^\circ$ ; the following were prepd. by heating to  $110-20^\circ$ : Ph, p- $\text{ClC}_6\text{H}_4$ , 35.4%, m.  $69-71^\circ$ ; p- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 92.3%, m.  $150-3^\circ$ ; p- $\text{ClC}_6\text{H}_4$ , p- $\text{ClC}_6\text{H}_4$ , 69.7%, m.  $109-11^\circ$ ; Ph, p- $\text{O}_2\text{NC}_6\text{H}_4$ <sup>(II)</sup>, 95.7%, m.  $157-60^\circ$ ; p- $\text{O}_2\text{NC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , 80%, m.  $161-3^\circ$ ; p- $\text{ClC}_6\text{H}_4$ , p- $\text{O}_2\text{NC}_6\text{H}_4$ , 89%, m.  $137-9^\circ$ . Heating the tri-Ph deriv. to  $230-40^\circ$  at 20 mm. gave 90% PhCN and a residue which with  $\text{NH}_4\text{OH}$  gave  $(\text{PhO})_2\text{PONH}_2$ . Similarly I gave m- $\text{O}_2\text{NC}_6\text{H}_4\text{CN}$  and  $(\text{PhO})_2\text{POCl}$ ; ~~XXXXXXXXXX~~ ~~XXXX~~ II gave PhCN and  $(\text{p-O}_2\text{NC}_6\text{H}_4\text{O})_2\text{POCl}$  which gave the ~~maxim~~ free acid, m.  $174-6^\circ$  on treatment with 2N NaOH and acidification. The acyls described above hydrolyzed completely in 2-2.5 hrs. in  $\text{H}_2\text{O}$  yielding 96-9%  $\text{RCONHPO}(\text{OR}')_2$

*Organophosphorus*

**Fluorine-containing trichlorophosphatesulfonaryls and their derivatives.**

L. M. Yagupel'skii and V. I. Troitskaya (Inst. Org. Chem., Acad. Sci., Kiev). Zhur. Obshchei Khim. 29, 552-6 (1959). cf. Kirsanov, this j. 22, 269 (1952). also cf. Olah and Pavlath, Acta chim. Acad. Sci. Hung., 4, 115 (1954).

Heating 0.1 mole  $p\text{-FC}_6\text{H}_4\text{SO}_2\text{NH}_2$  with 0.103 mole  $\text{PCl}_5$  at  $105-8^\circ$  1.5 hrs. gave after removal of excess  $\text{PCl}_5$  in vacuo and cooling, 99%  $p\text{-FC}_6\text{H}_4\text{SO}_2\text{N}:\text{PCl}_3$ , m.  $72-3^\circ$  (from petr. ether). This heated with equimolar amt. of  $\text{HCO}_2\text{H}$  in  $\text{C}_6\text{H}_6$  to  $85^\circ$  then left overnight gave 96.4%  $p\text{-FC}_6\text{H}_4\text{SO}_2\text{NHPOCl}_2$  (I), m.  $135-6^\circ$  (from  $\text{C}_6\text{H}_6$ ), while repetition of the process (1.5 hr. at  $80-5^\circ$ ) gave 86.5%  $p\text{-FC}_6\text{H}_4\text{SO}_2\text{NHPO(OH)}_2$  (OH)Cl, m.  $123-4^\circ$  (from  $\text{C}_6\text{H}_6$ ). Heating 0.01 mole I and 0.01 mole  $\text{HCO}_2\text{H}$  in 10 ml.  $\text{C}_6\text{H}_6$  1.5 hrs. at  $80-5^\circ$ , addn. of 0.01 mole  $\text{HCO}_2\text{H}$  and heating 4 hrs. longer gave on cooling 39%  $p\text{-FC}_6\text{H}_4\text{SO}_2\text{NHPO(OH)}_2$ , m.  $148-9^\circ$ . Stirring 29.2 g.  $\text{PhCF}_3$  and 25 g. 62% oleum 2 hrs. at  $0^\circ$ , keeping 1 day at room temp. and quenching in satd. NaCl at  $0^\circ$  gave 88.2% crude product of  $m\text{-F}_3\text{CC}_6\text{H}_4\text{SO}_3\text{Na}$ ; this with  $\text{PCl}_5$  gave 65%  $m\text{-F}_3\text{CC}_6\text{H}_4\text{SO}_2\text{Cl}$ , b.  $88-90^\circ$ , which with  $\text{NH}_3$  in  $\text{C}_6\text{H}_6$  gave 88% amide, m.  $121-2^\circ$ . This with  $\text{PCl}_5$  as above gave 99%  $m\text{-F}_3\text{CC}_6\text{H}_4\text{SO}_2\text{N}:\text{PCl}_3$ , m.  $52-4^\circ$  (from petr. ether); this gave, as above,  $m\text{-F}_3\text{CC}_6\text{H}_4\text{SO}_2\text{NHPOCl}_2$ , 84.5%, m.  $82-3^\circ$ , and  $m\text{-F}_3\text{CC}_6\text{H}_4\text{SO}_2\text{NHPO(OH)}_2$ , m.  $135-6^\circ$ , this being prepd. best by keeping the trichloride in a vessel over  $\text{H}_2\text{O}$  1 week. Treatment of the trichlorides with RNa in RON at  $0-5^\circ$ , finally 0.5 hr. at room temp. gave after extn. with  $\text{H}_2\text{O}$  and acidification of the aq. ext., a ppt. of the di-ester, and the org. layer on evapn. gave the triesters shown below:  $\text{AC}_6\text{H}_4\text{SO}_2\text{N}:\text{P(OR)}_3$  (A and R shown resp.):  $p\text{-F}$ , Me, 36.3%, m.  $45-6^\circ$  (from  $\text{C}_6\text{H}_6$ -petr. ether);  $p\text{-F}$ , Et, 65.2%, b.  $202-4^\circ$ ;  $p\text{-F}$ , Ph, 23.8%, m.  $69-70^\circ$  (from aq. EtOH);  $p\text{-F}$ ,  $p\text{-FC}_6\text{H}_4$ , 37.2%, m.  $70-2^\circ$  (from aq. EtOH);  $p\text{-F}$ ,  $p\text{-ClC}_6\text{H}_4$ , 53.5%, m.  $115-16^\circ$ ;  $p\text{-F}$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4$ , 80%, m.  $180-1^\circ$  (from  $\text{C}_6\text{H}_6$ );  $m\text{-CF}_3$ , Me, 59%, m.  $58-60^\circ$ ;  $m\text{-CF}_3$ , Et, 85.8%, b.  $185-7^\circ$ ;  $m\text{-CF}_3$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4$ , 84.2%, m.  $167-8^\circ$ ;  $\text{AC}_6\text{H}_4\text{SO}_2\text{NHPO(OR)}_2$ :  $p\text{-F}$ , Me, 66.5%, m.  $145-6^\circ$  (from  $\text{C}_6\text{H}_6$ );  $p\text{-F}$ , Et, 80.8%, m.  $118-19^\circ$ ;  $p\text{-F}$ , Ph, 12.7%, m.  $183-4^\circ$ ;  $p\text{-F}$ ,  $p\text{-FC}_6\text{H}_4$ , 14.2%, m.  $142-3^\circ$ ;  $p\text{-F}$ ,  $p\text{-ClC}_6\text{H}_4$ , 6.2%, m.  $149-50^\circ$  (the above 3 compds. were isolated from the prepn. of tri-esters above);  $p\text{-F}$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4$ , 88.6%, m.  $177-8^\circ$ ;  $m\text{-CF}_3$ , Me, 22.5%, m.  $93-4^\circ$ ;  $m\text{-CF}_3$ ,

Et, 91.3%, m. 71-3°; *m*-CF<sub>3</sub>, *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 88%, m. 194-5°. The di-esters above were best prepd. from the trichloride and 4.5 moles RONA in RON; the esters of phenols were prepd. best by addn. of 6 g.at. Na in C<sub>6</sub>H<sub>6</sub> to the trichloride followed by 6 moles ArOH in dioxane and refluxing until all Na had reacted after which the soln. was added to 2 moles trichloride in C<sub>6</sub>H<sub>6</sub> at 20° and was kept 1 hr. The nitrophenol deriva. were prepd. from the Na salt of the phenol in dry C<sub>6</sub>H<sub>6</sub>; this yielded the triaryloxy esters, which saponified with aq. alc. Na<sub>2</sub>CO<sub>3</sub> ( followed by acidification ) to the di-esters shown above. A slight insecticidal activity was found in *p*-FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N:P(OMe)<sub>3</sub> and the *m*-CF<sub>3</sub> analog.

**Phenyldichlorophosphazenesulfenaryls.***Organophosphorus*

V. I. Shevchenko and Zh. V. Morkuleva (Metallurg. Inst., Dnepropetrovsk). Zhur. Obshchei Khim. 29, 1005-8 (1959). cf. Kirsanov, this j. 27, 1253 (1957). Heating an equimolar mixt. of  $\text{PhPCl}_2$  and  $\text{ArSO}_2\text{NH}_2$  to  $70-5^\circ$  (or higher, depending on the m.p. of the amide) 15-20 min. results in loss of  $\text{HCl}$ , whose removal is then facilitated by blowing with dry  $\text{CO}_2$ . The residual solid or oily  $\text{ArSO}_2\text{N}:\text{PPhCl}_2$  was rubbed with dry  $\text{Et}_2\text{O}$  and chilled, to produce the crystalline products, which may be recrystallized from  $\text{Et}_2\text{O}$  or  $\text{EtOAc}$ . The following list describes unrecrystallized products, since the recrystn. raises the m.pt. only slightly and the crude products are already quite pure: (Ar shown): Ph, 80%, m.  $47-9^\circ$ ; o-tolyl, 101%, oil; p-tolyl, 101.5%, oil; p- $\text{ClC}_6\text{H}_4$ , 102% oil; o- $\text{O}_2\text{NC}_6\text{H}_4$ , 92.5%, m.  $73-5^\circ$ ; m- $\text{O}_2\text{NC}_6\text{H}_4$ , 93%, m.  $99-100^\circ$ ; p- $\text{O}_2\text{NC}_6\text{H}_4$ , 90%, m.  $171-4^\circ$ ; 1- $\text{C}_{10}\text{H}_7$ , 82%, m.  $99-102^\circ$ ; 2- $\text{C}_{10}\text{H}_7$ , 101.2%, resinous solid. The products may be prepd. also by addn. of an equimolar amount of  $\text{ArSO}_2\text{NNaCl}$  to  $\text{PhPCl}_2$  in  $\text{C}_6\text{H}_6$ ; the solvent is necessary to moderate the reaction. Addn. of the  $\text{PhSO}_2\text{N}:\text{PPhCl}_2$  to 3 moles  $\text{NaOH}$  in  $\text{MeOH}-\text{C}_6\text{H}_6$ , heating 0.5 hr. at  $50^\circ$ , followed by removal of the solvents in vacuo, and treatment with  $\text{H}_2\text{O}$  and dil.  $\text{HCl}$ , whereupon  $\text{PhSO}_2\text{NHP}(=\text{O})\text{PhOMe}$ , m.  $172-3^\circ$ , is formed in 75% yield.